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THE CAPACITY OF PAPER CONDENSERS AND TELEPHONE CABLES, WITH A NOTE ON THE DETERMINATION OF THE SPECIFIC INDUCTIVE CAPACITY OF DIELECTRICS.

By Anthony Zeleny and A. P. Andrews.

THIS paper gives experimental results showing the difference between the free charge capacity[1] of paper condensers and telephone cables and the capacity value that is obtained by the ordinary method where the galvanometer remains in the circuit during the whole period of its throw. The rate at which the absorbed charge is liberated immediately after the discharge of the free electricity was determined, and from it the true value of the free charge obtained. Attention is called, also, to a method of determining the specific inductive capacity of dielectrics.

1. The Discharge Key.

On account of the comparatively large absorption in paper condensers and telephone cables, it was found desirable to employ a key which enables the time the condenser is allowed to discharge to be accurately adjusted. The key consists of two keys operated by a swinging pendulum similar to that described by Carhart and Patterson.[2] The two wooden arcs over which the pendulum swings are divided into spaces representing known periods of time, the

[1] A. Zeleny, Phys. Rev., Vol. 22, p. 65, 1906.

[2] Carhart and Patterson, Electrical Measurements, p. 107, 1900.

shortest space being equivalent to .002 second. In Fig. 1, the keys and the connections are shown in a position in which the battery B is charging the condenser C. When the pendulum (not shown) is caused to swing, it first strikes the release bar of the key K_1, releasing the spring, which, on striking the upper stop, closes the galvanometer circuit. The condenser then discharges until the pendulum releases the spring of the key K_2. The time of discharge is dependent on the separation of the two keys, which are movable and clamped each to one of the graduated wooden arcs. Since the condenser begins to discharge when the spring of key K_1 touches

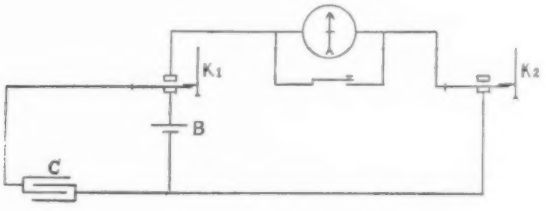


Fig. 1.

the upper stop, while the circuit is opened as soon as the spring of the second key is released, the position of the keys in which the time of discharge is zero must be determined experimentally.

When the key K_1 had the simple construction shown in Fig. 1, the time required to discharge the free charge of the condenser was found to be about twice the theoretical value. This was due principally, no doubt, to the vibration of the spring on striking the upper stop, so that the discharge, instead of being continuous, was intermittent. After many unsuccessful attempts to avoid this vibration, a key with a mercury contact was adopted. This is shown in Fig. 2. When the bar A is held in the position shown, the condenser is being charged, and when the release bar R is thrown down by the pendulum, the amalgamated point E is plunged into the mercury at B by the downward pull of the spring S. The disk D fits over the top of the mercury cup and prevents the loss of mercury by spattering. The spring H serves to make a metallic contact with the bar A. Even with this key, the time to discharge the whole measurable part of the free charge was still somewhat greater than demanded by theory.

2. Mica Condenser.

The data of Table I. give the throws obtained from a Leeds and Northrup condenser when using different times of discharge. These were taken for the purpose of making a comparison with the paper

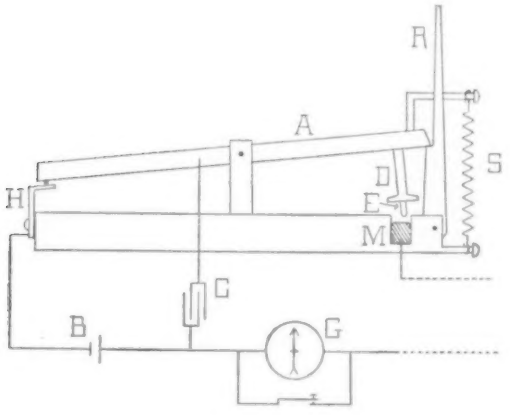


Fig. 2.

condensers and telephone cables. The capacity was one microfarad; the E.M.F., 4.076 volts; the quarter period of the galvanometer throw, 2.00 seconds; the resistance of the galvanometer circuit, 517.1 ohms.

Table I.

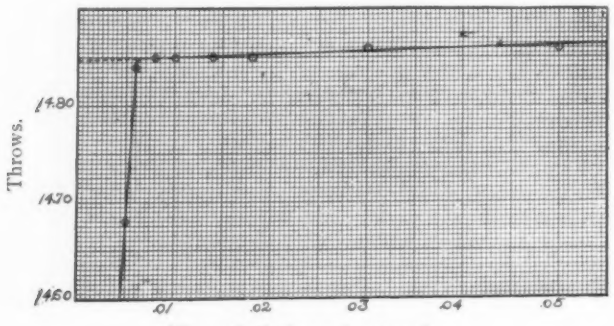
Time in Seconds.	Throws.
.005	14.68
.006	14.84
.008	14.85
.010	14.85
.014	14.85
.018	14.85
.030	14.86
.050	14.86
.150	14.88
2.000	14.96

The curve of Fig. 3, obtained from a part of the above data, shows that all the measurable part of the free charge was discharged in .008 second. The curve shows, also, that the increment due to the liberation of the absorbed charge amounts to .02 per cent. of the free charge for every .01 second that the condenser is allowed to

discharge. This holds true for many hundredths of a second, but becomes much less after a comparatively long interval. In two seconds the total increment was 0.76 per cent.

3. PAPER CONDENSERS.

On account of their large absorbing power, most paper condensers require a comparatively long time for charging. In some cases, with the particular apparatus employed, it was found necessary to



Time of discharge in seconds.

Fig. 3.

charge thirty seconds before the free charge became independent of the time of charging. The charge obtained increased at first with the time of charging owing to the absorption continuing during the discharge of the condenser and to a smaller amount of the absorbed charge being liberated. On this account, it was found convenient

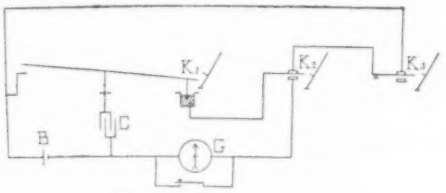


Fig. 4.

to introduce a third key which closed the condenser-battery circuit immediately after the opening of the galvanometer circuit. The required connections are shown in Fig. 4, in which K_3 is this third key, and K_1 the diagrammatic representation of the key shown in Fig. 2.

The throws obtained for various times of discharge from different condensers made by the same firm,[1] are shown in Table II. The

[1] Western Electric Co., Chicago.

nominal capacity of each of the condensers was two microfarads, and the charging electromotive force, 3.057 volts. The period of the

TABLE II.

Time in Seconds.	5.4	10	11	13	14
.008	12.61	13.30	12.98	15.30	14.84
.010	13.79	13.63	13.29	16.28	15.74
.012	14.04	13.68	13.38	16.42	15.86
.020	14.16	13.77	13.49	16.51	15.90
.030	14.21	13.82	13.55	16.53	15.92
.040	14.25	13.88	13.59	16.55	15.94
.050	14.28	13.90	13.63	16.56	15.95
.100	14.38	14.07	13.79	16.58	15.97
.150	14.47	14.17	13.91	16.60	15.99
.200	14.51	14.27	14.00	16.61	16.00
3.45	15.25	15.87	15.30	16.82	16.15

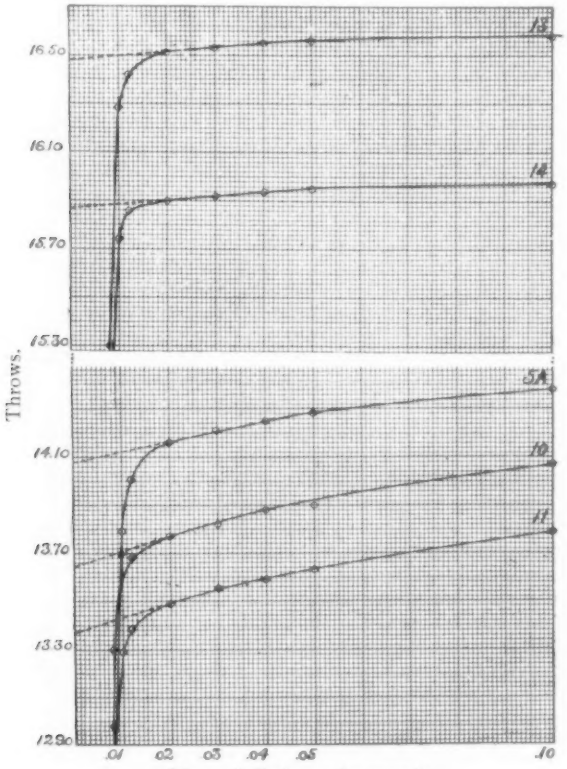


Fig. 5.

galvanometer throw was increased to 3.45 seconds by suspending weights from the coil. The discharge curves are plotted in Fig 5.

Several condensers made by different firms were also compared. The throws obtained are given in Table III.

TABLE III.

Time in Seconds.	5[1]	10[2]	2[3]	M[4]
.008	11.11	13.30	10.99	11.94
.010	11.24	13.63	12.24	12.61
.012		13.68	12.32	13.05
.015	11.48		12.44	
.020	11.66	13.77	12.57	14.38
.030	11.85	13.82	12.80	15.63
.040	12.05	13.88	12.95	
.050	12.18	13.90	13.09	17.26
.100	12.78	14.07	13.57	20.04
.150	13.08	14.17	13.96	21.98
.200	13.61	14.27	14.24	23.38
2.00	17.77			
3.45		15.87	20.35	47.74

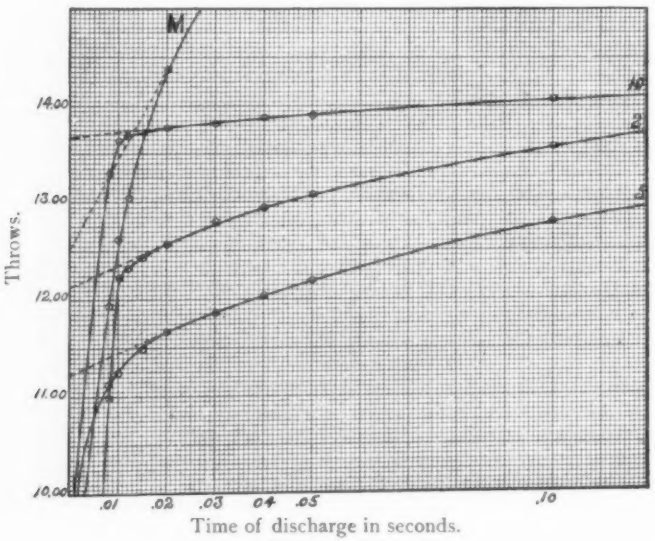


Fig. 6.

[1] Kellog Switchboard and Supply Co.
[2] Western Electric Co.
[3] Stromberg-Carlson Telephone Manufacturing Co.
[4] Marshall, a very old condenser used about fifteen years.

The data for condenser No. 5 were obtained with a different suspension than was employed with the other condensers. The curves are plotted in Fig. 6.

4. Telephone Cables.

Discharges were taken in a similar manner from a paper telephone cable[1] 1,500 feet in length containing fifty pairs of wires. The wires were connected so as to obtain the capacity of the pairs in parallel. The throws are given in Table IV., and the curve is plotted in Fig. 7. The charging electromotive force was 1.019 volts and the quarter period of the galvanometer, 2.50 seconds.

Table IV.

Time.	d	Time.	d
.003	16.88	.080	17.33
.005	16.98	.120	17.44
.010	17.02	.150	17.48
.015	17.09	.200	17.57
.020	17.11	.250	17.62
.030	17.17	.270	17.65
.040	17.19	2.50	18.66
.050	17.23		

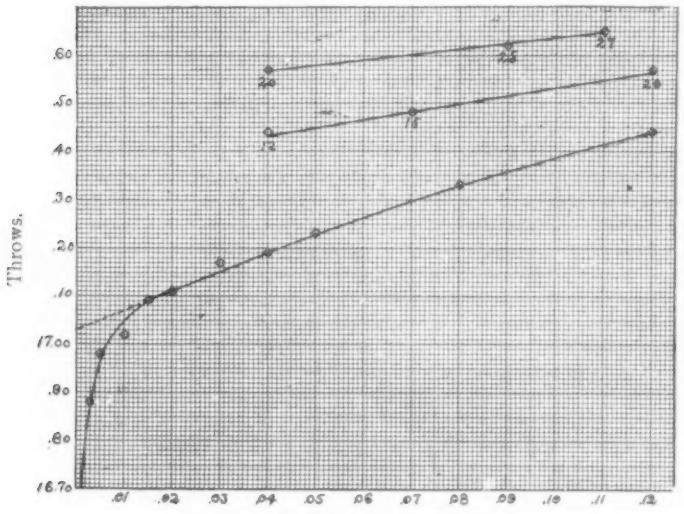


Fig. 7.

[1] John A. Roebling Sons Co.

5. "TRUE," "FREE CHARGE," "ORDINARY" AND "EFFECTVE" CAPACITIES.

Each of the preceding curves shows that after the free electricity is discharged the liberated absorbed charge continues to flow at almost a uniform rate for a considerable time. Each of the straight lines representing this is projected backward in the figure as a dotted line until it meets the axis of ordinates. The ordinate of the point where the dotted line leaves the curve represents the whole measurable part of the free charge of the condenser together with that part of the absorbed charge that is liberated during this discharge. On the assumption that the absorbed charge is liberated at the same rate during the time the free electricity is discharging as it is liberated immediately after, the point at which the dotted line cuts the axis of ordinates represents[1] the true free charge of the condenser. As previously suggested by one of us,[2] the "*true*" capacity is obtained from the true free charge; the "*free charge*" capacity, from the free charge with the addition of the absorbed charge that is liberated during the discharge of the free charge; the "*ordinary*" capacity, from the quantity discharged when the condenser remains connected to the galvanometer during the whole period of its throw; and the "*effective*" capacity, from the quantity obtained under any other condition of employment. Each of these four has its distinct use.

TABLE V.

Condensers.	Period of Throw in Seconds.	"Free Charge" Capacity Greater Than the True Value, in Per Cent.	"Ordinary" Capacity Greater Than the True Value, in Per Cent.	Absorbed Charge Liberated in .or", in Per Cent. of the True Free Charge.
Mica.	2.00	.01	.76	.02
13	3.45	.18	2.06	.09
14	3.45	.25	1.84	.12
Cable.	2.50	.35	9.58	.23
5*A*	3.45	.57	8.31	.28
11	3.45	.90	14.43	.45
10	3.45	.95	16.35	.48
2	3.45	3.54	67.6	1.77
5	2.00	3.92	58.4	1.96
M	3.45	14.86	281.3	7.43

[1] This may be modified slightly, no doubt, after the rate is investigated at which the absorbed charge is liberated during the discharge of the free electricity.

[2] A. Zeleny, PHYS. REV., loc. cit.

Table V. gives the per cent. by which the "*free charge*" and the "*ordinary*" capacity values are greater than the "*true*" capacity values of the condensers considered in this paper. It also gives the rate at which the absorbed charge is liberated immediately after the discharge of the free electricity.

6. Specific Inductive Capacity of Dielectrics.

The specific inductive capacity of dielectrics is now ordinarily determined by the alternating current methods. The capacity values obtained by these methods approximate to the "free charge"

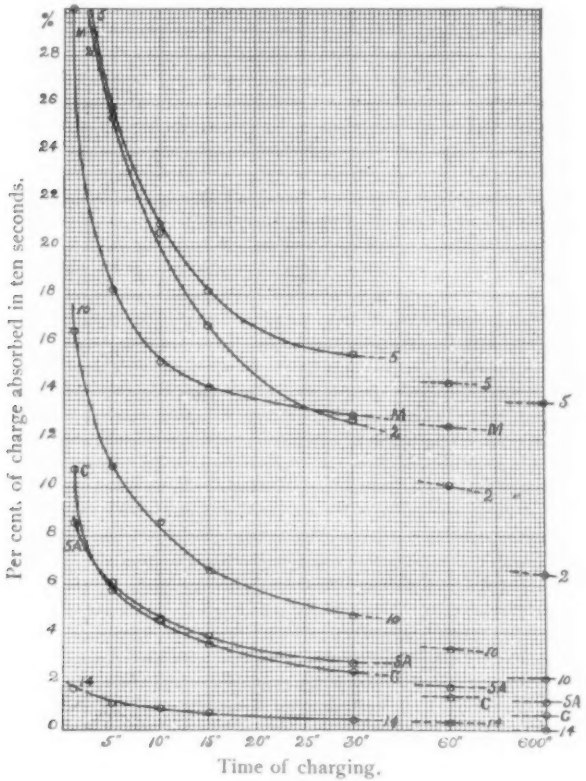


Fig. 8.

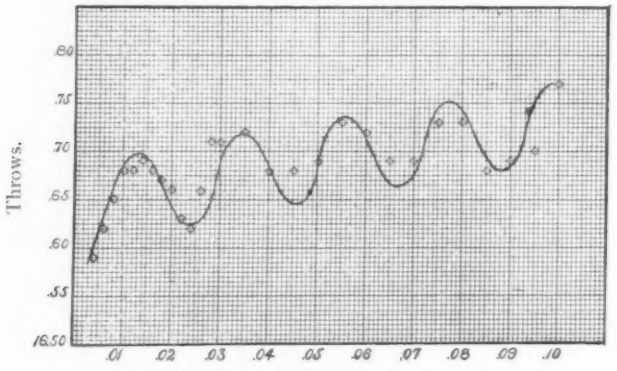
capacities as here considered. The "true" capacity determines the value of the specific inductive capacity and this may differ appreciably from the value obtained by the alternating current methods.

7. ABSORPTION CURVES.

The curves of Fig. 8 show the relation between the time of charging and the per cent. of the total charge absorbed when the condenser is allowed to stand ten seconds before it is discharged. The condensers were short-circuited between each reading. The curves bear the same numbers as the condensers to which they belong. These curves are not corrected for the surface leakage or the conduction of the dielectric. The object in obtaining them was to show the great difference in the absorbing power of different paper condensers and that this continues for a long time, rendering inaccurate the leakage method of measuring their resistance even when the charging is continued for a considerable time.

8. WEIGHTED GALVANOMETER COIL.

During the progress of these experiments a weighted galvanometer coil was employed which gave for the mica condenser the curious curve shown in Fig. 9. The weights consisted of lead balls



Time of discharge in seconds.

Fig. 9.

held at a distance from the coil by means of a brass wire. The impulse given to the coil set the balls into rapid invisible vibrations of small amplitude which caused the coil to vibrate, creating alternating surges of electricity in it. If the surge was in the same direction as the condenser discharge at the instant the galvanometer circuit was opened, the throw was increased, and if the surge was in the opposite direction, diminished. In this manner the sine curve

was obtained with its maxima at intervals corresponding to the period of vibration. This is given to show the danger of using coils with attachments that are not sufficiently rigid.

9. Summary and Conclusion.

The value of the capacity of paper condensers as obtained by the ordinary direct deflection method is larger than the true capacity value by an amount which in the condensers here employed varies from 1.8 to 281 per cent., the amount depending on the condenser and on the period of the galvanometer. In a paper telephone cable the increment was found to be 9.58 per cent. when the quarter period of the galvanometer was 2.50 seconds.

Since the condensers and telephone cables are employed with alternating currents where the effective capacity has approximately the free charge value, the ordinary method of measurement that is almost universally employed must be discarded even for commercial purposes.

The value of the true free charge gives the measure of the "true" capacity of a condenser and should be employed in the calculation of the specific inductive capacity of dielectrics.

Physical Laboratory,
University of Minnesota,
March 10, 1908.

SOME ELECTRICAL PROPERTIES OF SILICON.

BY FRANCES G. WICK.

III. THE HALL EFFECT IN SILICON AT ORDINARY AND LOW TEMPERATURES.

THE study of the Hall effect is the third of a series of experiments upon the metallic silicon produced by the Carborundum Company. The first investigations were upon the thermo-electric behavior [1] and the second upon the resistance [2] of this same material.

A thin plate of silicon was placed between the poles of an electromagnet and a current was passed through the plate in a direction perpendicular to the magnetic force. A permanent electromotive force was thus established which had a direction perpendicular to the magnetic force and also perpendicular to the primary current in the plate. This phenomenon, known as the Hall effect, which occurs in all metals to a certain extent, was observed in silicon.

The measurement of the Hall effect offered the same difficulties that have been met in the other work upon silicon. The substance is hard and brittle and not easily fused. Thin plates such as were needed in this work were difficult to make and the connections were also troublesome. The extremely large thermal E.M.F. was a source of disturbance and the work had to be carried on in such a way as to prevent unequal heating of the silicon. The sources of error were, however, avoided or eliminated to such an extent that the results obtained were checked a number of times indicating considerable accuracy.

Since the effect is more easily measured in thin plates it was desirable to make the silicon plates as thin as possible. On account of the brittleness of the material, plates cast from the fused metal were broken before they could be taken from the mould into which

[1] Wick, Frances G., PHYS. REV., Vol. XXV., No. 5, Nov., 1907.
[2] Wick, Frances G., PHYS. REV., Vol. XXVII., No. 1.

the material was poured. An attempt was made to saw sections from a mass of silicon by means of a thin motor-run emery wheel working under water. This shattered the edge of the wheel and made very little impression upon the silicon. Finally two plates were ground down from irregular pieces of silicon by the use of carborundum powder upon an iron wheel. Plate I. was ground from a choice specimen of silicon 99 per cent. pure, very compact and showing crystalline structure, which was kindly furnished by Mr. Tone, of The Carborundum Company. Plate II. was of silicon produced several years ago. This material was not so compact as that of the other plate nor of such a high degree of purity. The analysis of this product is given as follows:

Si	95.30 per cent.
Fe	1.06
Al	1.61
C	2.10
CaO	.33

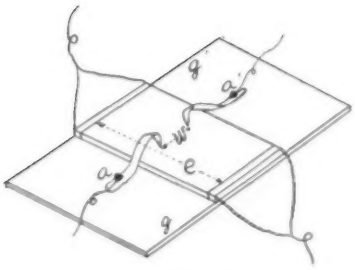


Fig. 1.

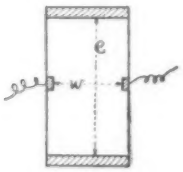


Fig. 2.

Plate I. was mounted upon glass with DeKhotinsky cement. In Fig. 1, *gg'* represents the strip of glass upon which the metal plate was mounted. Two spring contacts fastened to the glass by rivets *aa'* made the side connections to the plate. The end contacts were made by copper plating each end of the plate and soldering to this a very thin strip of copper.

The contacts to Plate II. (Fig. 2) were made by copper plating the ends and a small spot at the center of each side. Fine copper wire was soldered to this for side connections and thin sheet copper for end contacts.

Table I. gives the dimensions of these plates.

TABLE I.

	Thickness of Plate.	Total Width of Plate.	Width Between Side Contacts. W	Total Length.	Length Between End Contacts. l
Plate I.	.7409 mm.	1.8 cm.	1.48 cm.	3.35 cm.	3 cm.
" II.	1.3056 mm.	1.6 cm.	.92 cm.	3.5 cm.	2.7 cm.

The apparatus was set up as indicated in Fig. 3. The plate pp' was placed between the poles of an electromagnet in such a way

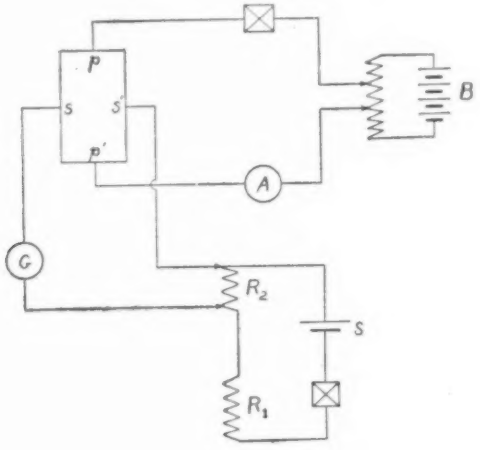


Fig. 3.

that the magnetic lines of force were perpendicular to it. The pole pieces used were placed about 1.5 cm. apart so that a strong uniform field could be obtained.

The determination of the intensity of this field was made by comparison with one of known value at the center of a long solenoid. Two circular turns of wire 3.6 cm. in diameter were placed between the poles of the magnet and the direction of the current in the magnet reversed. The deflection of the galvanometer was observed. A solenoid 90.8 cm. long and 2.6 cm. in outer diameter of four layers of wire was used as the primary of a comparison field. A coil of fine wire 11 cm. long placed at the center of the

primary was used as a secondary. The current was reversed in the primary and the throw produced by the current induced in the secondary observed. The field between the poles of the magnet was found by comparison. The following equation is true :

$$\frac{\delta}{\delta'} = \frac{\varphi A}{\varphi' A'}$$

A = effective area of coil between magnet poles.

φ = field between poles of magnet.

δ = deflection produced in coil by reversing current in magnet.

A' = effective area of secondary of comparison field.

φ' = field at center of solenoid.

δ' = deflection produced by current in secondary when current in primary was reversed.

Substituting in the above formula particular values of the known field and corresponding galvanometer deflections the following result was obtained :

$$\varphi = \delta \times 475.97.$$

TABLE II.

Current in Amperes.	Galvanometer Deflection.			Magnetic Field. C.G.S. ϕ
	Upon Reversing Field in One Direction.	Upon Reversing Field in Opposite Direction.	Average. δ	
5.153	5.4	5.4	5.4	2,570
6.125	5.5	6	5.55	2,641
6.813	5.7	5.7	5.7	2,713
9.125	6	6	6	2,855
10.063	6.2	6.2	6.2	2,951
10.625	6.3	6.3	6.3	2,998

Table II. gives the field between the magnetic poles for a number of different current values. A calibration curve was drawn from which the field strength corresponding to any current might be obtained.

A current shunted from a storage battery B (Fig. 3) was passed longitudinally through the plate between p and p'. To measure the transverse current through the plate the points SS' were connected to a galvanometer circuit in such a way that the circuit included a known resistance (R_2) shunted from a standard cell circuit.

A D'Arsonval galvanometer of the Sullivan type was used for these measurements. An attempt was made to use a weak field Thomson instrument of greater sensibility but the magnetic disturbances due to the street cars and various other sources were such as to make the use of this instrument impossible.

A longitudinal current through the plate between p and p' produces a difference of potential at points along parallel edges of the plate such as S and S', unless they are exactly opposite. By adjusting R_2 any difference of this sort may be compensated for by the current from the standard cell S until there is no deflection of the galvanometer. The resistance R_1 was so high that the E.M.F. of the standard cell remained constant on closed circuit.

Another necessary precaution was the prevention of any inductive effect upon the galvanometer circuit due to the action of the magnet when the current through it was turned on or off. This was accomplished by carefully twisting the wires leading from S and S' and by the addition of adjustable loops if necessary.

The Hall effect was measured as follows: A current from the storage battery B was passed through the plate between p and p'. Then the magnetizing current was started so as to develop lines of force perpendicular to the plate. An E.M.F. due to the Hall effect was then generated between S and S' and produced a deflection of the galvanometer. The direction of this E.M.F. was changed by reversing the polarity of the magnet or by changing the direction of the current from the storage cells through the plate. The magnitude of the effect was measured by changing the resistance R_2 sufficiently to restore a balance and bring the galvanometer to rest in the position it occupied before the magnetic circuit was closed. The E.M.F. produced by the action of the magnetic lines of force upon the current was then easily computed.

An attempt was made to determine the dependance of the effect upon the strength of the current through the plate and the intensity of the field, but the results were not satisfactory because less current through the plate and a weaker magnetic field produced no measurable effect upon the galvanometer used. The current through the plate could not be greatly increased without heating the plate and producing thermal effects which were larger than the Hall effect.

In order to compare the results obtained with those for other

TABLE III.

Plate I. Thickness (d) = .07409 *cm. E.M.F. of Standard Cadmium Cell* = 1.0189 *volts. Increase in* R_2 *when magnetic current is turned on indicates a field in one direction; decrease, in the other direction.*

R_1	Resistance of Standard Cell. r	R_2 Magnetic Current Off.	On.	Av.	Change in R_2 for Balance. R_3	Current Through Standard Cell Circuits. $\left(\frac{1.0189}{R_1 + r + R_2}\right)$ i	Transverse E.M.F. Generated by Action of Magnet on Sil. Plate $(i \times R_3 \times 10^8)$ e (C.G.S.)	Main Current Through Plate. I (C.G.S.)	Current Through Magnet in Amperes. c	Magnetic Field from Curve. M (C.G.S.)	Rotary Coefficient of Hall Effect. ed/IM
10,000	1,527	6.5	5.3	5.9	1.2	$.8834 \times 10^{-4}$	1.060×10^{4}	.002677	6.75	2,685	109.3
10,000	1,527	8.5	9.7	9.1	1.2	$.8832 \times 10^{-4}$	1.060×10^{4}	.002677	7	2,725	107.6
60,000	1,263	52	59.8	55.9	7.8	$.1661 \times 10^{-4}$	1.296×10^{4}	.002650	6.875	2,695	134.4
60,000	1,263	51	46.5	48.75	4.5	$.1662 \times 10^{-4}$	$.7478 \times 10^{4}$	.002650	7	2,725	76.7
100,000	1,041	108.5	122	115.25	13.5	$.1007 \times 10^{-4}$	1.360×10^{4}	.002650	7.075	2,745	138.1
100,000	1,041	112	100	106	12	$.1007 \times 10^{-4}$	1.209×10^{4}	.002650	6.95	2,700	125.1
100,000	1,041	113	127	120	14	$.1007 \times 10^{-4}$	1.410×10^{4}	.002693	6.875	2,695	145.5
100,000	1,041	112	100	106	12	$.1007 \times 10^{-4}$	1.209×10^{4}	.002675	6.875	2,695	124.2
									Average		120.1

substances the rotary power was computed in the usual way as indicated below.

$$\text{Rotary power} = \frac{ed}{IM}.$$

M = strength of magnetic field in C.G.S. units.
I = strength of primary current in C.G.S. units.
e = transverse E.M.F. in C.G.S. units.
d = thickness of plate in cm.

TABLE IV.

Plate II. Thickness (d) = .13056 *cm. E.M.F. of Standard Clark Cell* = 1.429.

R_1	R_2			R_3 (Av.)	i	e	I	C	M	$\frac{ed}{IM}$
	Current on.	Current off.	Av.							
99,200	21	15								
	22	27.9	21.5	5.95	1.437×10^{-5}	8.551×10^{3}	.01477	6.5	2,668	28.4
	39	49								
	37	27								
99,200	34.5	24.5	35.2	10	1.437×10^{-5}	14.37×10^{3}	.02438	10.26	2,970	25.8
	25	17.5								
99,200	25	33	25.1	7.75	1.437×10^{-5}	11.14×10^{3}	.01749	10.66	3,200	25.9
	50	34								
99,200	42	54	45	14	1.437×10^{-5}	20.12×10^{3}	.029	10.26	2,965	31.6
	23.5	17.5								
	24.5	17								
99,200	24.5	32	23.2	7	1.437×10^{-5}	10.06×10^{3}	.016695	8.208	2,790	28.2
									Average =	28.0

Tables III. and IV. give the data necessary for this computation and the results obtained for Plates I. and II. The sign of the Hall effect on silicon is negative according to the convention used in these values. The rotary power is considered positive when a positive transverse current is generated in the plate in that direction in which the conducting strip tends to move under the action of the main current and the magnetic force.

Fig. 4 indicates the absolute direction when the main current flows upward. The direction of the effect in silicon is the same as that in gold.

EFFECT OF LOW TEMPERATURE.

In order to determine the effect of temperature upon the Hall effect in silicon, Plate I. was cooled to a temperature of $-100°$ C. and the effect compared with that at ordinary temperatures.

The silicon plate was fastened to a copper strip 5.3 cm. wide and 3 mm. thick, the glass to which it was fastened serving as insulation (Fig. 5). The copper was adjusted so that the end to which the silicon was fastened was placed between the poles of the electromagnet. The lower part of the copper plate extended into a Dewar bulb containing liquid air.

The temperature obtained was measured by means of a thermo-junction.

The ratio of galvanometer deflections at room temperature and at $-100°$ was taken to indicate relative values of the Hall effect at these temperatures. The current through the electromagnet was

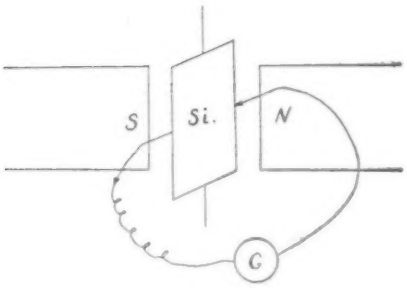


Fig. 4.

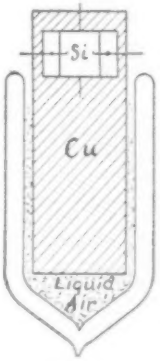


Fig. 5.

kept unchanged at the two temperatures and that through the plate was adjusted to the same value. This adjustment was necessary since the increase in resistance at the lower temperature caused a corresponding decrease in current. The resistances R_1 and R_2 were the same in both cases.

Table V. gives deflections produced at room temperatures and at $-100°$.

The difference in potential due to the Hall effect decreases as the temperature is lowered. At $-100°$ the effect is .496 that at room temperature. In some substances such as tellurium the effect increases at low temperatures. Bismuth shows an increase to a point of inflection at about $-50°$ C., then a decrease. A peculiarity with regard to the Hall effect in silicon is not inconsistent with other physical properties of the substance. The resistance is very

TABLE V.

Galvanometer Deflections Produced by the Same Magnetic Field and Primary Current through the Plate at Ordinary and Low Temperatures. $R_1 = 9{,}000$. $R_2 = 0$.

Room Temperature. Galvanometer Deflection.		Temperature = −100° C. Galvanometer Deflection.	
Field in a Given Direction.	Field in Opposite Direction.	Field in a Given Direction.	Field in Opposite Direction.
4	3	1	1
3	2.7	1.1	1.2
3	2.7	.7	1.5
4	3	1	
2.7	2.5	1.3	
3	1.5		
3	2.5	1.5	2
2.7	2	1.8	
3.3	2.5	1.2	
2.8	3	1.5	
3	2.3	1.5	
2		1.5	
2		1.2	
3		1	
2		1.5	
3.2			
2.8			
2.9			
Av. = 2.911	2.518	1.271	1.425

Average deflection = 2.7145. Average deflection = 1.348.

Ratio of deflection at −100° to that at room temperature $= \frac{1.348}{2.7145} = .496$.

high and the temperature coefficient negative. The thermal electromotive force is extremely large.

RELATION BETWEEN HALL EFFECT AND THERMOELECTRICITY.

Dr. J. C. Beattie in a paper, "On the Relation between the Hall Effect and Thermoelectricity in Bismuth and in Various Alloys," [1] found, in these substances, a very close connection between the two phenomena. Metals which occupy an extreme position thermoelectrically have a correspondingly extreme position as regards Hall effect. This is true of bismuth and tellurium and Dr. Beattie predicted that this relation would hold for other substances.

[1] Beattie, J. C., Proc. Roy. Soc. Edin., 1895–96.

He gives the following list of metals arranged in a thermoelectric series given by Wiedemann.[1]

TABLE VI.

Metal.	Rotary Coefficient of Hall Effect.	Thermoelectric Power at 20° C.
Silicon 99 per cent. pure	− 120.2	
Silicon 95 per cent. pure	− 28.0	− 400
Bismuth	− 10.1	− 89
Cobalt	+ 0.00459	− 22
Nickel	− 0.0242	− 15.5 (at 50°)
German silver	− 0.00053	− 11.75
Palladium	− 0.00115	− 6.9
Aluminium	− 0.00038	− 0.68
Lead	+ 0.00009	0
Tin	− 0.00004	+ 0.1
Copper	− 0.00052	+ 3.8
Platinum	− 0.00024	+ 0.9
Gold	− 0.00071	+ 1.2
Silver	− 0.00083	− 3
Zinc	+ 0.00041	+ 3.7
Cadmium	+ 0.00055	+ 3.48
Iron	+ 0.0113	+ 17.5
Antimony	+ 0.192	+ 22.6
Tellurium	+ 532.000	+ 502

In the second column is given the direction and magnitude of the Hall effect according to the results of Ettinghausen and Nernst.[2] In a third column has been added the values of thermoelectric power taken from the Smithsonian tables. The results obtained for silicon have also been inserted. This substance verifies Dr. Beattie's prediction both as regards direction and approximate magnitude. The thermal E.M.F. is larger than that of bismuth and in the same direction. This is also true of the rotary coefficient of the Hall effect.

A further relation was traced for bismuth showing that with change in temperature there is a corresponding variation in Hall effect and thermoelectric power. That such a relation holds in the case of silicon upon reduction of the temperature to — 100° is evi-

[1] Wiedemann's Lehre von der Electricität, Bd. II.

[2] Sitzungsberichte der Kaiserlichen Akademie zu Wien, 1886.

dent from the curves[1] showing the thermoelectric power of this substance. The Hall effect is smaller at this low temperature being .496 its value at room temperature. The thermoelectric power is also less — about .75 of its value at 20° C. While the proportionality is not strictly true, the relation is evident.

The plate which contains the least impurity (Plate I.) has the larger Hall effect, indicating that the presence of foreign substances tends to diminish the effect.

The physical properties of silicon are of such a peculiarly interesting nature that it would be highly desirable, in work of this sort, to have chemically pure material. Thus far it has been impossible to get such metallic silicon in quantities. At the suggestion of Professor Nichols, the author has tried various methods of obtaining pure material and of getting the amorphous silicon into a form which could be used for the investigation of physical properties. Further experiments would be necessary to determine the value of these processes.

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[1] Wick, Frances G., PHYS. REV., Vol. XXV., No. 5, p. 389.

EFFECT OF THE CATHODE RAYS IN CHANGING THE COLORS OF CERTAIN MINERALS.

By C. C. Hutchins.

SOME twelve years since it was observed that if green or colorless fluorite were subjected to the action of the cathode ray in a vacuum, the color of the mineral was changed. The matter has been somewhat farther investigated with the following results.

A straight glass tube about 15 cm. long and 2 cm. in diameter is furnished with a flat disc electrode at either end and midway with an aluminum shelf. A side tube with ground-in joint serves to introduce and remove the specimens, which rest upon the shelf, opposite the cathode.

A high vacuum being produced in the tube the minerals are bombarded in the cathode stream. The current is kept low so as not to unduly heat the tube or minerals.

Fluorite.

The most common varieties of this mineral are colorless, green and amethyst. By the action of the cathode ray the colorless and green are quickly changed to the amethyst variety.

If the vacuum be high and the current weak the change penetrates deeply into the mineral. With a lower vacuum or stronger current the penetration is not as deep but the surface coloration more intense, at length becoming bronzed, and looking exactly as though a solution of violet analine had been allowed to dry upon the surface of the mineral. In the latter case the surface being ground or chipped away, the unchanged mineral is found below. It is interesting to note that at all stages the color produced by the cathode ray is indistinguishable from that of the native mineral, differing only in intensity.

Tourmaline.

Tourmalines from Paris, Maine, and a few neighboring localities are commonly pink or green in color; the two colors not infre-

quently being united in the same crystal. In this case the crystal may shade from nearly colorless at one end through various tints of pink into light and dark green at the other end. A crystal pale pink in color was broken in two; one piece kept for comparison, and the other treated in the vacuum tube for twenty minutes. At the end of that time the pink tint of the treated fragment had changed to the characteristic tourmaline-green. The crystal was not very transparent, but the change seemed to be complete throughout, so that further treatment produced no further visible change. The change was not the effect of heat; for when the untreated half was heated for half an hour no change was produced in it. Both parts were boiled together in nitric acid, washed and dried, without producing alteration in either.

CORUNDUM.

A semi-transparent crystal of this mineral was broken into three pieces. One piece was kept for comparison, the second was treated for five minutes and the third for twenty minutes.

The original color of the specimen was not uniform, being bluish in spots and in others reddish — the general effect being light purple. The change in tint even in the piece receiving the shorter treatment was unmistakable; so that the three pieces being placed in the hand of a person who knew nothing about the matter, he instantly distinguished among them, pronouncing the longest treated piece the palest of the three.

The imperfect transparency of the specimen does not permit much more to be added. No change was produced by subsequent heating and boiling in nitric acid.

When the color of a mineral depends upon some chemical admixture the fact is often revealed by its fluorescence; which at the same time is a very delicate test of such admixture. For instance: fragments of green and flesh-colored apatite were treated together in the tube; the green fluoresced green and the flesh-colored red, but the color of neither was changed by the treatment.

Again: a bit of perfectly transparent and nearly colorless cyanite fluoresced yellow, and with remarkable brilliancy surpassing willemite even. A piece only 0.5 sq. cm. in area gave sufficient light

to enable the reading of a watch nearly a meter distant. On the other hand the ordinary blue cyanite fluoresces red, almost exactly like corundum.

The action of the cathode ray in affecting mineral coloration brings to mind the recently discovered action of radium emanation upon the corundum minerals, and strongly suggests that some minerals have been changed while in the earth by radio-activity.

The fact that fluorite is often found in alternate crystalized bands of colorless and amethyst, and that the tourmaline is bi-colored, may be in some way connected with the pyro-electric properties of the minerals — known to be particularly marked in tourmaline. I have left a small heap of moderately active radium on a transparent fluorite plate for eight months but no visible change has yet been produced. The same radium has colored pink the glass tube in which it is kept. One may not infrequently find fragments of glass, originally white, changed to the same color that radium imparts to glass, by merely lying long exposed in contact with the earth. I am told that in our southwestern deserts the change is effected with comparative rapidity.

I now publish the above notes in the hope that some one having better and more extensive material than is at my command may take up and pursue the matter.

BOWDOIN COLLEGE,
BRUNSWICK, MAINE,
January 23, 1908.

LIQUID ABOVE THE CRITICAL TEMPERATURE.[1]

BY W. P. BRADLEY, A. W. BROWNE AND C. F. HALE.

IF the wide glass pressure tube of a Cailletet liquefaction apparatus be filled with pure carbon dioxide [2] and compressed, not too slowly, into progressively smaller volume, while the bath is maintained constant at some point below the critical temperature, at a certain volume the eye of the observer may notice a series of phenomena due to liquefaction.

Beginning usually at the level of the top of the mercury column, a thin, transparent cylindrical sheath mounts upward in immediate contact with the walls of the glass tube, loses width when it strikes the curve at the top of the tube, then closes together at the point. This appearance is due of course to the wetting of the interior walls of the tube. Under the circumstances named, the liquid cannot be seen to form anywhere else than on the walls of the tube, except indeed occasionally on the mercury meniscus, if the latter has sufficient area. The reason is clear. While the volume is decreasing, heat of compression maintains all of the gas at a higher temperature than that of the bath. The disparity of temperature between gas and bath is greatest in the center of the tube, and least at the walls, which conduct away the heat.[3] When the volume corresponding to incipient liquefaction is reached, liquid forms in that part of the gas which is coolest — that is, on the

[1] The subject-matter of the present paper was suggested by some observations which were made during an investigation of the effect of mechanical shock upon carbon dioxide near the critical temperature. (PHYS. REV., 19, 1904, 258–272; 26, 470–482, 1908.) It may properly be considered as part of the inquiry named, which was assisted by Grant No. 104 from the Elizabeth Thompson Science Fund.

[2] The gas used in these experiments contained impurity, unabsorbed by potassium hydroxide solution, equal to 1 part by volume in from 30,000 to 40,000. (Cf. Journal of the American Chemical Society, 30, 1090–1096, 1908.)

[3] It will be apparent that these phenomena are much more pronounced in wide tubes than in narrow ones. Our pressure tube was of 6 mm. internal diameter. (Loc. cit., p. 263.)

walls. Moreover it begins to form at that point on the walls which is cooled, in a sense, both without and within — that is, at the level of the top of the mercury meniscus — and ends at the point most affected by the heat of compression — namely, the tip of the tube, against which the convection currents set up by the heated central core of the gas are directed.[1] The process is simply a progressive wetting of the internal glass surface from below upwards.

Almost immediately the liquid can be observed flowing down the walls in ripples, which present much the same appearance as that of water flowing down a roof, or a spent wave receding on the beach.

If the initial volume is considerably greater than the volume of saturation and the compression is checked sharply at the appearance of the ripples, no accumulated liquid can be detected, as a rule, when thermal equilibrium is again established between the carbon dioxide and the bath. On the other hand when the gas is saturated, and there is any liquid present before compression, the quantity of the latter is notably increased by the newly formed liquid which flows down into it.

The new liquid of course is always warmer than that into which it runs, and therefore less dense. If there is but little of it, and its speed down the walls is slight, it stops at the meniscus or not far below. If there is considerable of it and it rushes down the glass, it penetrates more deeply below the surface, leaving the glass however after it reaches the meniscus, and curving inward more and more as it diffuses into the older liquid. In either case, its course after striking the meniscus can be followed for a little by the "striæ" or lines of differential refraction which appear. Naturally the diffusion is seen at its best when there is considerable of the older liquid present.

Another phenomenon which may be noted by close scrutiny is a sort of agitation or tremulousness in the bottom of unsaturated gas just before the sheath "lifts" on the glass. This agitation seems to be limited to a few degrees below the critical temperature. When the bath temperature is 28° for instance, it is seen only occasionally and faintly, and close to the mercury, while it becomes

[1] Probably also the approximately hemispherical shape of the tip, presenting relatively less surface, contributes to the same result.

rapidly more pronounced, and may be seen at a greater height above the mercury, as temperatures nearer the critical are chosen.

There can be little doubt that the layer of gas next the mercury, being cooler than the entire system above it, is the first to feel the approach of saturation, and probably a liquid film forms on the mercury surface before it shoots up the glass. Unfortunately it was never possible to establish this priority by observation. In fact it was only once or twice that liquid was seen forming on the mercury surface at all. The difficulties of observation in this regard are very great, for liquefaction conducted on so small a scale.

Below the critical temperature these phenomena are very simply explained by the simultaneous presence of liquid and vapor in the carbon dioxide. *Every one of them persists above the critical temperature.* As will be shown, this is not only true qualitatively, but the quantitative changes which are brought about by rise of temperature present no discontinuity at the critical temperature.

The method of experimentation either above or below the critical temperature was as follows: The apparatus[1] was stationed in front of a north window so that the contents of the pressure tube could be observed by diffused, transmitted light. The gas having been already so far compressed that it was all directly subject to the influence of the bath, and the latter having been maintained sufficiently long at the desired temperature, the volume of the gas was noted. The observer then opened the needle valve to admit water slowly from the hydraulic pump into the pressure jacket of the apparatus. A dial gauge connected with the pressure jacket indicated the increase of the pressure of the carbon dioxide. In order that successive compressions might be comparable with one another in speed, an assistant read aloud the progress of the pointer around the dial, calling off equal intervals of pressure. With some practice the observer could so manipulate the needle valve as to raise the pressure not only very steadily during the course of each compression, but with practically equal speed in successive compressions. Whenever the speed became abnormal in either sense, the corresponding observation was rejected.

On the instant when the sheath of incipient liquefaction "lifted"

[1] Loc. cit., p. 263.

and the rippling commenced, the needle valve was shut and the system was allowed to stand until the carbon dioxide had regained the temperature of the bath. Its volume was then noted again. Thermal equilibrium was assumed to be reached when the pointer ceased to recede upon the dial of the gauge. The mechanical lag of the pointer was corrected by gentle tapping upon some effective spot upon the gauge.

Inasmuch as for a given initial volume the final volume varies somewhat with the speed of compression, successive readings of the final volume afforded a valuable check upon the uniformity of the speed, as well as upon the personal equation of the observer.

Readings of the final volume were secured for a series of initial volumes, which varied from the largest readable volume to that

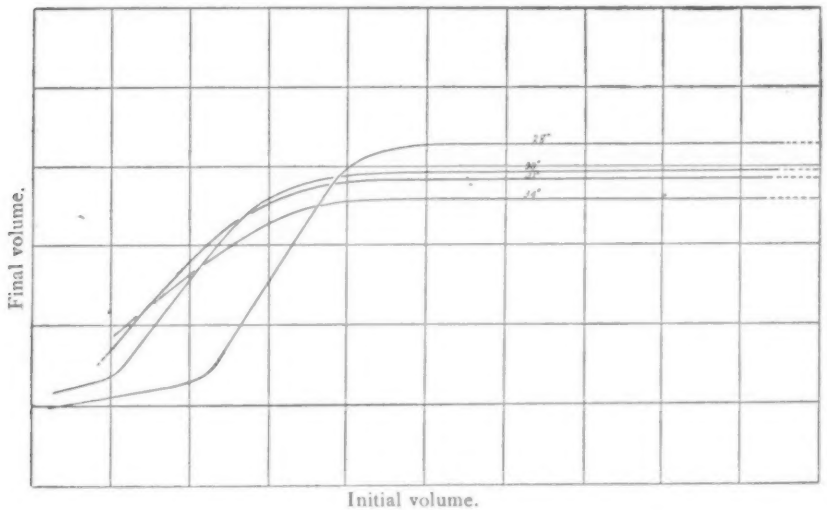

Fig. 1.

which represented nearly complete liquefaction. When one such series was complete the thermostat was adjusted to another temperature, for a second series, — and so on.

The results for four sample temperatures are given in the following table, and are plotted also in Fig. 1.

It will be noticed that the curves for all four of the temperatures begin (at the right) with a horizontal portion of considerable length. This rounds into a second rectilinear portion, which slopes in general

T.	Initial Vol. c.mm.	Final Vol. c.mm.	T.	Initial Vol. c.mm.	Final Vol. c.mm.
28°	578	267.5	31°	570.5	243.8
	385.5	263.2		403.4	242.3
	336.4	261		258	227.4
	291	240.2		204.4	194
	243.4	164		150.7	135.6
	190.8	112			
	112.5	99.5			
30°	575.5	247.8	34°	570.5	226.4
	325	248.6		459	228.5
	276	241.2		367.6	228.5
	239	218		278	225.4
	213.8	198.1		224.3	196
	185.5	162.4		183.4	168.5
	170.7	139		153.5	145.2
	139	114			
	114.1	108.1			

towards the origins of the axes. This portion in turn, in the case of the lower two temperatures, curves into a third rectilinear which is more nearly horizontal and ends abruptly when the initial and final volumes are approximately the same. For the two higher temperatures this approximate equality is reached at the end of the second rectilinear.

To understand the meaning of these ripple curves, let *XYZ*, in Fig. 2, be a liquefaction area, whose ordinates are pressures and whose abscissas are volumes, and let *ABCD* be the isothermal of any selected temperature below the critical. If the volume of gas at *A* be compressed with a measurably uniform velocity, all of the gas will become heated until the temperature gradient is such that the heat of compression flows outward into the bath as fast as it is produced. From the point where thermal equilibrium is reached the compression becomes isothermal, but its curve lies higher than that of the bath temperature. As the gas at the center of the compression tube will always be hotter during compression than that which is near the walls, its isothermal, considered separately, will be higher than that of the latter.

Let *bb'B'* represent the isothermal of the gas at the center, and for the sake of simplicity let it be assumed that the gas at the walls follows the isothermal of the bath temperature, *ABCD*, though this

of course would never be strictly true. If compression begins at A', $A'b'$ will represent the course of the gas at the center, and $A'a'$, the simultaneous course of gas at the walls. As the pressure at any given moment is necessarily the same on all the gas, a' and b' will be reached at the same moment. At a', liquefaction occurs, the valve is shut, and compression ceases. The total volume now remains constant. The gas at b', if alone, would fall vertically to the

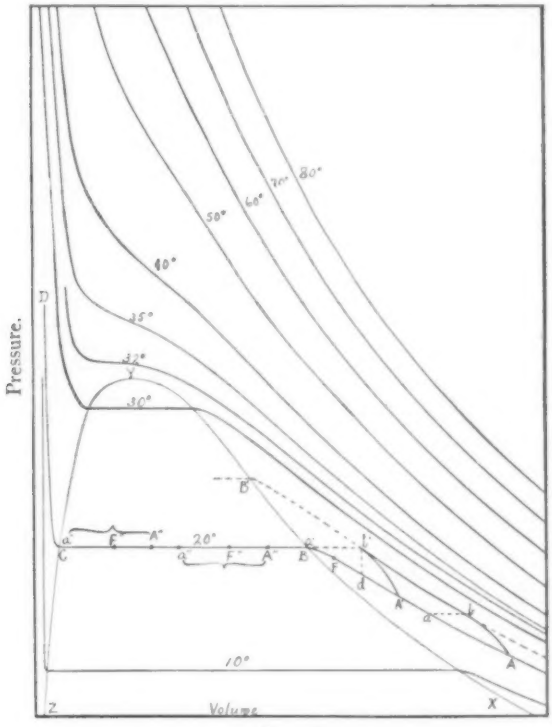

Fig. 2.

normal isothermal at d, but equilibrium will be reached when the system as a whole arrives at some point intermediate between a' and d, as F.

The point F will usually lie to the right of B, if (a) the compression valve is promptly closed at the appearance of liquid; (b) the compression tube is a wide one rather than capillary; (c) the rate of compression is not too slow; and (d) the walls conduct well. In

these experiments, indeed, residual liquid was never observed so long as the initial volume was considerably greater than the volume of saturation.

Fig. 2 makes clear also that, other things being equal, the points a' and b', and therefore F, are independent of the initial volume A so long as the latter is greater than A'. The situation so far is represented in Fig. 1 by the horizontal portion of the curves.

When A stands sufficiently far forward on the isothermal AB, gas near the walls will reach a' before the gas in the center has reached its own isothermal $bb'B'$ at all, but stands at some point on the isobar $a'b'$. The effect is to shift F more and more towards the saturation point B. This situation is represented in that portion of the curves of Fig. 1 which is concave to the axis of volumes.

Whenever the initial volume lies at the left of B, within the liquefaction area, and not too near C, gas at the center can never rise above the normal isothermal, assuming still that gas at the walls does not, and the sole effect of decrease in volume will be liquefaction of gas at the walls. The final volume will lie at F'' between a'', representing gas at the walls, and A'', representing gas at the center. Moreover, the distance $A''F''$ will be constant. In other words, there will always be an increase in the liquid volume after compression, and the ripple curve becomes rectilinear, sloping toward the origins of the axes.

When the initial volume is so near to C that a'' reaches C on its own isothermal, then the distance by which F'' is in advance of A'' decreases until A'' is so near to C that ripples are no longer seen at all. This condition is represented by that portion of the curves at the left in Fig. 1 which is rectilinear and not far from horizontal.

By similar means it becomes apparent why it is that at higher temperatures than the one just now chosen for discussion, the first horizontal of Fig. 1 is longer; that the second rectilinear becomes shorter; and that the last rectilinear becomes shorter and disappears as the all-liquid portion of the isotherm diverges more and more from a true vertical, and the distance BC becomes shorter than $A''a''$.

Regarding the ripple curve of 31° it should be noted that every time ripples were observed, the system as a whole was above the

critical temperature. This was shown by the appearance of the meniscus just before thermal equilibrium was established, after compression, between the carbon dioxide and the bath. This of course was when the initial volume was not too large, as explained above. Further, when the initial volume was small enough for the existence of some liquid, compression caused at one and the same time the disappearance of the meniscus and the appearance of ripples. The latter followed the curve of the glass just as always (a fact indicative of their liquid character), and could be followed sharply to a level which rose slowly higher than that of the vanished meniscus. Having arrived at this rising level, which was thus quite sharply defined though it was itself invisible, the ripples, still descending by their acquired momentum, left the glass, curved more and more inward toward the center of the tube, became rapidly thinner and so disappeared. Presently the meniscus appeared at a level just a little higher than that at which the last ripples bent away from the glass and disappeared by diffusion. All of the phenomena of ripple curve 31° down to the minutest detail were an exact duplication of those of the ripple curves for 28° and 30° with a single exception of the visible meniscus. In the latter two curves, if a suitable initial volume was chosen, ripples ran down *until they reached the rising meniscus* before diffusion and their disappearance began. In the 31° curve there was no meniscus at the top of the liquid until the rippling was over. But when the meniscus did finally appear it was found at the level where the conduct of the ripples indicated that it would be.

It was difficult for an observer not to believe that at a bath temperature of 31° ripples *of liquid* ran down the glass until they reached the top of *other liquid* like themselves, with which they mixed in the usual way, with corresponding increase in the total liquid volume. Indeed in all probability a doubt would never occur, except for the commonly accepted dogma that liquid cannot exist without its cap on! We shall recur to this point later.

Again, identically the same phenomena appeared at 31.5°, 33°, 34°, 36° and 38°, though of course there was no visible meniscus at any time at these temperatures. But by watching the conduct of the ripples one might follow the accumulation of "liquid" at

each temperature, from its beginnings at the mercury until the total volume was nearly all liquid, and ripples appeared only in the extreme tip of the pressure tube. Measurements of final volume above 34° were of doubtful value however, as the needle of our gauge ran beyond its scale, and the necessary check on the uniformity of the speed of compression was lacking.

Ripples which form above the critical temperature follow the glass just like those which form at temperatures below that point. Even those which form near the tip of the compression tube take the longer way outward along the glass, instead of flowing vertically downward through the lighter gas below them. When the initial volume is too large to admit of the accumulation of liquid, they run down the entire distance to the mercury without any loss of "body." When the initial volume is too small to admit of the presence of vapor, no ripples are seen at all under compression. At initial volumes lying between these two extremes, ripples run down to some characteristic level, which is lower for larger initial volumes and higher for smaller ones. Arrived at this level, wherever it may be, the ripples at once begin to leave the glass and quickly become invisible, giving every appearance in so doing of mixing with a medium of a density allied to their own.

Ripples alone, in a region where changes of density are very great and very rapid, might be accounted for without assuming any change of physical state, but such a group of phenomena as that given above can hardly be so explained. Above the critical temperature, as below it, the ripples must be considered as consisting of *liquid*, and they flow down until they reach the top of the other *liquid*, if any, which has accumulated as the result of previous compression. When the carbon dioxide is already all liquid, ripples naturally cannot form at all.

One more phenomenon observed above the critical temperature deserves mention. As has been said, the volume of invisible liquid lying on the mercury could be gauged with approximate accuracy by observing the level on the walls at which the ripples produced by compression ceased to increase in thickness, left the walls, and began to disappear.

This level having been determined, and the heat of compression

having been allowed to disappear, a slight *increase* of volume, quite insufficient to cool any part of the system down to the critical temperature, gave rise to ripples or striæ which appeared in the "liquid" volume, except near the walls, and which worked their way rather slowly upward through the liquid to its top, and then disappeared. As they rose, they tended somewhat to recede from the walls toward the center.

Now expansion is a cooling process. The cooling takes effect chiefly in the center of the carbon dioxide, rather than at the walls, which remain approximately at the temperature of the bath. *Falling* ripples or striæ in the center of the carbon dioxide might easily be accounted for, on the basis of the orthodox theory of the critical state, by convection currents in the "gas," of which the whole volume is thought to consist. *Upward* ripples, in the coolest part of the carbon dioxide, appearing only in the lower portion of the same and ceasing abruptly at a certain predetermined level, can apparently be accounted for only as the result of a change from a physical state of greater density to one of less — that is, from the liquid to gas or vapor.[1] Indeed this conclusion is strengthened by the fact that whenever the expansion was sufficient to cool the carbon dioxide below the critical temperature, so that the meniscus temporarily appeared, it appeared always where the compression ripples would have led one to expect it, and the upward current temporarily assumed the form of true bubbles, exceedingly minute but unmistakable. In the interval before the meniscus faded out again in consequence of the inflow of heat from the bath, these bubbles could be seen to rise toward the meniscus, and disappear if they reached it. If thermal conditions were such that the meniscus faded quickly, the fog of bubbles gave way again to ripples or striæ which likewise rose no further than the level where the meniscus had been.

When there was no "liquid" present, as shown by the flow of compression ripples down the glass quite to the mercury, no upward currents were ever produced by subsequent expansion. When the carbon dioxide was all "liquid," as shown by failure to obtain compression ripples because of the small initial volume, up-

[1] Cf. Ramsay, Philosophical Magazine, 16, 1883, 120.

ward currents, if produced at all by expansion, could be followed nearly or quite to the top of the tube. In any case intermediate between these extremes, the striæ, as already said, ceased upward at the same level as the compression ripples did downward, making of course due allowance for the small increase or decrease in the "liquid" volume caused by the very "condensation" or "evaporation" which was under observation.

Beginning with the classic work of Andrews[1] in 1869, there have continued to accumulate, with reference to the critical state, facts which are difficult or impossible to understand except on the assumption that liquid can exist above the critical temperature. Previous to this time it had been held for nearly half a century, and apparently without question, that the disappearance of the top of a liquid was sure proof that the liquid itself had ceased to exist; and it is perhaps in part because of the age and respectability of this traditional interpretation of the critical state that comparatively few venture seriously to oppose it even now.

It may not be out of place in this connection to call attention again to some of the typical experimental facts which are not in accord with the generally accepted theory.

I. The Course of the Isothermals for Temperatures not too High Above the Critical Temperature.

At the general region where liquefaction, if any, would be expected, these isothermals exhibit in sequence the same changes in the value of pv as occur below the critical temperature. They bend at first rapidly toward the axis of pressures, with a tendency to become perpendicular thereto, and afterwards reverse the curvature with a tendency to become parallel to the same. Below the critical temperature this means the passage into, and out of, an area of progressive liquefaction. Above the critical temperature, what else can it mean? Below the critical temperature liquid and vapor are discontinuous because of their limited solubility in each other. Therefore the liquid phase not only becomes localized because of its greater density, but it possesses a meniscus. Above the critical temperature the liquid and vapor are soluble or miscible in all pro-

[1] Philosophical Transactions, 159, 1869, 575–89.

portions. Whether the two are stratified in obedience to their respective densities or not, there can never be a meniscus. If stratification exists, it is not apparent to the eye in the usual way, and it is always a temporary phenomenon subject to the ordinary laws of diffusion.

II. Andrews'[1] "Continuity" Experiment.

Carbon dioxide is heated first to a temperature above the critical temperature and is then subjected to a pressure greater than the critical pressure. No liquefaction is observed. Then with constant pressure the "gas" is cooled below the critical temperature. Still no visible liquefaction. However, the carbon dioxide must now be *all liquid*, for the pressure is in excess of that required for liquefaction at the present temperature. And in fact it *is* all liquid, as becomes evident by the violent ebulition which occurs throughout the entire mass when the pressure is released. *Somewhere* during the process all of the gas has changed to liquid, but at no point has it been possible to see the liquid, or, let us rather say, at no point has it been possible to see the top or any other surface of liquid.

The explanation of the paradox is easy, once the possibility of the existence of liquid above the critical temperature is granted.

Beginning at that part of the compression, above the critical temperature, where the isothermals begin to curve towards the axis of pressure, liquefaction occurred, and copiously. As the liquid so formed is perfectly miscible with the vapor which remains, it does not become localized, with a visible surface to it.[2] Liquefaction would not be complete at this stage, except under excessive pressures. In the second stage of the experiment, while the carbon dioxide was cooling toward the critical temperature, and while the pressure continued greater than the critical pressure, liquefaction became complete. The temperature at which this could occur depends on the pressure. From that temperature downward there could of course be no expectation of a surface to the liquid other than that of the containing walls.

[1] Loc. cit.

[2] This is the point where liquefaction would have been betrayed by ripples, in a wide tube; but Andrews' tube was capillary.

III. EXPERIMENTS BY WHICH THE SOLVENT POWER OF INVISIBLE LIQUID IS MADE TO REVEAL THE PRESENCE OF THE LATTER.

The experiment of Hannay and Hogarth[1] is a typical one in this class. A solution of potassium iodide in alcohol was heated above the critical temperature, and the potassium iodide did *not* fall tumbling to the bottom throughout the entire former liquid volume as soon as the meniscus disappeared, though it ought to have done so if the orthodox view of the critical temperature is correct. No solid whatever appeared even at 380°, or 140° above the critical temperature of alcohol. Instead of explaining this fact by assuming that liquid alcohol was still present in the tube though not visible, it was assumed that, at sufficiently high pressures, gaseous alcohol dissolves potassium iodide.

This otherwise unsupported hypothesis was directly contradicted however by other observations of Hannay and Hogarth. If a hot iron rod was held close to the side of the hot tube, crystals formed on the inner surface of the glass, next to the rod. It is quite clear that the extra heat supplied locally by the rod could not have lessened the pressure in the tube. Doubtless it did evaporate liquid alcohol locally. It was observed further that if the volume of the solution at 350° was suddenly increased, a precipitation of solid occurred, which disappeared again when the pressure was restored. But the increase of volume was calculated to evaporate liquid alcohol, while the sudden expansion would temporarily cool that which remained and so decrease its solvent power. Altschul[2] afterward showed that a *general* precipitation of potassium iodide began at 356°. This is doubtless the temperature at which, by progressive evaporation of invisible liquid alcohol, his solution of potassium iodide became saturated. Probably the solution was more concentrated at the start than that of Hannay and Hogarth.

IV. The belt of irregular refraction in an undisturbed Natterer tube at the level of the vanished meniscus, showing a lighter medium above and a denser one below. The belt grows broader of course by diffusion, and in time disappears, even when the temperature is constant.

[1] Chemical News, 40, 1879, 256; 41, 1880, 103–6.

[2] Zeitschrift für comprimirte und flüssige Gase, I., 1898, 207–8.

V. The striæ observed when a Natterer tube which is above the critical temperature, and which has hitherto been undisturbed in its vertical position, is turned end for end. These are indicative of the mixing of miscible media of different densities, and their appearance is identical with that observed when a similar tube completely filled with stratified alcohol and water is inverted.

VI. That an undisturbed Natterer tube, cooled from a higher temperature to the critical, shows first a fog belt, then the meniscus suddenly in the midst of it, while one whose contents have been well mixed above the critical temperature shows fog through its entire length under the same circumstances. In the one case the liquid has the opportunity of remaining localized when the critical temperature is exceeded, except indeed for gradual diffusion. Naturally the depth of the fog belt, which precedes the meniscus, varies in this case with the time which has been available for diffusion. In the other case the whole liquid has a chance to mix completely with the vapor — and takes it.

VII. Experiments which show directly the persistence of differences of density as between the upper and lower portions of an undisturbed two-phase system after the critical temperature has been passed. From this very comprehensive class may perhaps be selected that of Cailletet and Collardeau with the so-called O-tube ;[1] that of de Heen with his modified Natterer tube, separable by a valve into two parts ;[2] and that of Teichner with his little glass floats of varying buoyancy.[3] In this class belong also the ripple phenomena of this paper, and the definition of the vapor-liquid boundary by means of fog produced by mechanical vibration, as described in a former article.[4]

Much of the confusion now existing between the two schools of thought regarding the nature of the critical state appears to be due to a difference in the methods of observation. Those who hold to the newer view, that liquid persists above the critical temperature, base their belief principally on experiments like those catalogued above — experiments in which the pressure tube is purposely left

[1] Comptes Rendus, 102, 1886, 1202–7.

[2] Zeitschrift für comprimirte und flüssige Gase, 2, 1898, 97.

[3] Zeitschrift für anorganische Chemie, 37, 1903, 232.

[4] PHYS. REV., 26, 470–482, 1908.

undisturbed by any external influence while the thermal changes are taking place and where the observations are made within a reasonable time after the critical temperature has passed.

Those who hold to the older view, that at the critical temperature homogeneity ensues, find their warrant: (*a*) in experiments in which either the critical temperature is reached and passed with extreme slowness or the observations are made after the system has remained standing in thermal equilibrium for long periods after the critical temperature is passed, so that the effect of more or less complete diffusion is felt, or (*b*) in experiments in which the substance under examination is purposely given opportunity to mix, either by frequent inversions of the tube, or by the use of a mechanical stirrer inside.

Precisely the same confusion would arise over the critical solution temperature of an acetone-water system under the same circumstances. Each school is right as to its own facts, but the only theory so far which seems to include all the facts is that which assumes that at the critical temperature the miscibility of liquid and vapor ceases to be limited. This theory which has been proposed more than once[1] during the last generation, has recently found its sturdiest champion in Julius Traube.[2] Deserving of special emphasis is Traube's distinction between real *liquid* (liquidons) and the *liquid phase*, and between real *gas* (gasons) and the *vapor phase* respectively, whereby the liquid phase is to be understood as true liquid (liquidons) containing true gas (gasons) in solution — and the vapor phase as true gas (gasons) containing true liquid (liquidons) in solution.

[1] Jamin, Comptes Rendus, 96, 1883, 1448.

Cailletet and Collardeau, Annales de Chimie et de Physique (6), 18, 1889, 269.

Batelli, Atti del Reale Istituto Veneto di scienze, lettere e arti, 50, 1893, 1615.

Wesendonck, Naturwissenschaftliche Rundschau, 9, 1894, 209.

Dwelshauvers-Dery, Bulletin de l'Academie royale de Belgique (3), 30, 1895, 570.

Pictet, Zeitschrift für comprimirte und flüssige Gase, 1, 1897, 63. Cf. also p. 207.

de Heen, Zeitschrift für comprimirte und flüssige Gase, 2, 1898, 97. Bulletin de l'Academie royale de Belgique, 1907, 859.

Ramsay and Steele, Zeitschrift für physikalische Chemie, 44, 1903, 378. Cf. Proceedings of the Royal Society, 30, 1880, 323; 31, 194. Philosophical Magazine (5), 37, 1894, 215.

[2] Zeitschrift für anorganische Chemie, 37, 1903, 225; 38, 1904, 399.

The proportion of gasons to liquidons in the liquid phase, and the proportion of liquidons to gasons in the vapor phase, is limited below the critical temperature by the existence of a saturation point. Above the critical temperature there is no such limit. Above the critical temperature solutions of different densities, because of different degrees of concentration, may still be stratified by various means, but such a condition is subject to the influence of gradual diffusion, just as is the case when two liquids, of different densities but perfect miscibility, are similarly stratified.

This view transforms the "area of liquefaction" on a diagram of isothermals into an "area of saturation." Outside of this area of saturation, on the side opposite the axis of pressures, liquid (liquidons) may exist, less or more according to volume, but never to the extent of saturating the gas (gasons) in which it is dissolved. Outside of the same area, but on the side next to the axis of pressures, gas (gasons) may still exist, more or less, according to volume, but never to the extent of saturating the liquid (liquidons) in which it is dissolved. Above the critical temperature, true liquid and true gas may exist side by side in any proportion, according to volume, but there can never be phases except in the loose sense of temporary stratification.

Outside of the area of saturation there is perfect continuity in every direction. The area of saturation, indeed, is after all only an exceptional case in an otherwise general continuity between the liquid and gaseous conditions of matter. Andrews' distinction between gas and vapor in terms of the critical temperature may still be retained, if the capacity for continuity is made fundamental, but not otherwise. An aëroform substance is "gas" above the critical temperature, and "vapor" below that temperature. Whether as "gas" or "vapor" it may be changed to liquid by pressure alone — as "gas," with perfect continuity, — as "vapor," only by a discontinuous process involving saturation.

Summary.

1. The phenomenon of "rippling," which is observed in the wide glass compression tube of a Cailletet apparatus when the volume of saturated vapor is decreased, shows no discontinuity at the critical

temperature, but may be observed in detail, under corresponding conditions, at temperatures up to 38°, and probably higher. These ripples flow downwards in the vapor phase, adhering to the glass.

2. An increase in the volume of localized "liquid" results, above the critical temperature, in ripples or striæ which flow upward, without any tendency to adhere to glass but rather the opposite, till they reach the localized "vapor." Below the critical temperature these ripples or striæ are replaced by bubbles, rising to the meniscus. There is no break in this phenomenon at the critical temperature, except as to definiteness of outline.

3. Résumé of the evidence for the existence of liquid above the critical temperature; and a discussion of divergent views concerning the nature of the critical state, in favor of the theory of complete mutual solubility of the liquid and gas.

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THE FLUORESCENCE AND MAGNETIC ROTATION SPECTRA OF POTASSIUM VAPOR.

By R. W. Wood and T. S. Carter.

Introduction.

RECENT study of the optical properties of sodium vapor[1] by one of the present writers, has shown that our knowledge of the structure of the molecule and of the mechanism of radiation may be increased by the investigation of metallic vapors at comparatively low temperatures. During the investigation the periodicities of the vibrating mechanisms were studied in a number of ways: by absorption, by exciting the vapor with white or monochromatic light, by cathode ray stimulation, and from the standpoint of the magneto-optical properties of the vapor. The fluorescence spectrum which appears when the non-luminous vapor is stimulated by white light, is very complex, and resembles many emission band spectra.

A method was found, however, by which it was possible to analyze this complex spectrum into a number of simpler spectra, each one of which could be made to appear at will by exciting the vapor with a monochromatic source of radiation of the proper frequency. The vapor can be excited to fluorescence by monochromatic sources obtained by utilizing certain lines from the arcs of various metals such as zinc, cadmium, thalium, lead, silver, bismuth and copper. In each case a series of lines is obtained, the lines of the series being very nearly equidistant.

It was further found that any given series of lines could be brought out by exciting the fluorescence with a source of radiation of wavelength corresponding to that of any line in the series, but that certain lines were sometimes absent depending upon the point of excitation.

Sodium vapor in a strong magnetic field has the property of

[1] R. W. Wood, Phil. Mag., Nov., 1906.

rotating the plane of polarization of light for wave-lengths corresponding to those of certain lines in its absorption spectra, *i. e.*, polarized light, which has been passed through magnetized sodium vapor and a Nicol's prism (set orginally for the complete extinction of light) gives a bright line spectrum consisting of a large number of sharp lines. Each bright line corresponds to a dark line in the absorption spectrum (or more exactly to wave-lengths very close to it) but it was found only a very small percentage of the absorption lines showed, this rotatory power. There are only about 100 strong lines in this spectrum, which has been called the magnetic rotation spectrum, while there are some 2,500 lines in the same region in the absorption spectrum. The magnetic rotation spectrum resembles very closely the fluorescent spectrum excited by white light, athough there are fewer lines in it. The intensities of the lines are very variable, and apparently bear no relation to the intensities of the corresponding absorption lines.

Five or six distinct series of equidistant lines have been identified in the magnetic rotation spectrum, and these appear to correspond to the series in the fluorescent spectrum brought out by monochromatic stimulation, though they are not coincident with any which have been obtained thus far.

In view of the similarity between the emission spectra of sodium and potassium, it was thought very desirable to extend to potassium vapor studies along the same line.

HISTORICAL.

The red fluorescence which is exhibited by the vapor of metallic potassium when it is illuminated with a beam of white light was first observed by Wiedemann & Schmidt.[1]

The metal was enclosed in an exhausted glass bulb heated until vaporization occurred, and a strong beam of sun or arc-light focused at the center of the bulb. A red cone of fluorescent light appeared, which, when examined with the spectroscope, showed a red band, the position of which as roughly determined was between wave-lengths 695 and 615 $\mu\mu$.

[1] Wied. Ann., 57, 447, 1896.

General Facts.

The vapor has been studied from the standpoint of its absorption, fluorescence, and selective magnetic rotation of the plane of polarization, and it has been possible to obtain photographs of these spectra.

One of the most interesting facts brought out by these investigations is the close resemblance between the spectra of potassium vapor and the corresponding spectra which have been observed in the case of sodium.

During the early part of the experiments the vapor was investigated in glass bulbs of from 5 to 10 centimeters diameter. A very small piece of metal was rolled up and introduced into the bulb, which was then exhausted to a vacuum of about 1 millimeter, and sealed. During a preliminary study of the conditions under which the fluorescence was exhibited to the best advantage it was found that the glass bulb became blackened after being heated for a very short time. Bulbs of hard glass, blown in an oxyhydrogen flame were then tried and found fairly satisfactory.

Fluorescent Spectrum.

Method and Apparatus. — The fluorescent light of the vapor was first examined with a two-prism Steinheil spectroscope. The spectrum showed a broad bright band with apparently no structure far out in the red. In order to obtain greater dispersion the light was next examined by means of a large three-prism spectrograph. With this apparatus the spectrum showed some structure. Examined visually about fifteen bands could be distinguished. By studying the condition carefully it was finally possible to get the fluorescence bright enough to yield fairly satisfactory spectrograms on the new Wratten & Wainwright panchromatic plates with exposures of from two to three hours.

The best photograph taken with a width of slit such that the *D* lines were just resolved on the plate showed that the spectrum was fluted, the flutings, however, not being resolved in the lines. The bands were quite sharp on the sides toward the shorter wave-lengths and on the other sides terminated in wings which extended with gradually decreasing intensity up to the head of the next band.

The absorption spectrum photographed with the same apparatus was found to be the complement of the fluorescent spectrum. When the two negatives were superimposed it was seen that each dark band of the latter was represented by a light band in the former. As it was desirable to work with a much denser vapor than it was possible to obtain with the glass bulbs, the behavior of the metal when heated in a highly exhausted steel tube was studied.

A small piece of metallic potassium was placed at the center of a piece of thin steel tubing, 2 inches in diameter and 24 inches in length. The ends were closed with glass plates, cemented to the tube with sealing wax, and the whole exhausted with a Fleuss pump, through a small lateral tube, brazed into the steel wall.

Arc-light, sent in in a slightly oblique direction, was brought to a focus by means of a lens directly over the metal. On heating the tube the red spot of fluorescent light was observed through the opposite end.

The fluorescence was much more intense than had ever been observed with the vapor in the glass bulb, being of about the intensity and color of a Bunsen flame heavily charged with pure lithium chloride.

The arrangement of the apparatus during the subsequent experiments on the fluorescence was exactly similar to that employed in the work on sodium vapor. The apparatus consisted of a tube of thin steel 3″ in diameter and 30″ in length containing a steel retort, made by fitting two circular disks of steel to a short piece of tubing, slightly smaller than the long tube. The ends of the retort were provided with small oval apertures. The metal was cut up into strips and introduced into the retort, which was pushed to the center of the tube and the plate glass ends cemented on. The tube was then exhausted to a pressure of 1 mm. and heated at its center with a Bunsen flame. The illuminating beam of arc-light was brought to a focus just inside of one of the apertures of the retort. By sending the exciting light in an oblique direction through one end, the fluorescence could be observed through the same end against a dark background. With the metal in the retort, which prevented its rapid distillation to the colder parts of the tube, it was possible to make exposures of practically any length. The ends

of the tube were kept cool by jackets of absorbent cotton, which dipped into pails of water.

By employing higher dispersion an attempt was made to break up the bands which had been photographed with the three-prism spectrograph. The prisms were removed from that apparatus and a plane grating substituted. It was found that this new apparatus gave a first order spectrum about five times as long as the spectrum given by the prisms. The lenses used were of 36-inch focal length. The adjustment was so made that the center of the spectrum fell at the axis of collimation and very good definition was obtained throughout.

With this arrangement of things several very good photographs of the spectrum were obtained. The time of exposure varied from two to three hours. It was possible to measure on the dividing engine the wave-lengths of about fifty lines by comparing them with standard lines in the iron spectrum. They extend from wave-length 6346 to 6767. It was found that the centers of these bands could be determined to within half an Ångstrom unit. In the region of shorter wave-lengths the bands are all of about the same intensity, and are nearly equally spaced along the spectrum. Between 6415 and 6670 there are eight very strong lines which are about equally distant. They are represented in the magnetic rotation spectrum and are due to the strongest lines in the absorption spectrum. This series will be discussed further under the magnetic rotation spectrum. As we go out into the region of longer wave-lengths the spectrum consists of groups of lines of nearly the same intensity, the lines between the groups becoming fainter and fainter. The lines of this spectrum coincide line by line with the principal lines in the absorption spectrum, although as will be seen, there are a great many more absorption lines. The wave-lengths of the fluorescence lines measured are given below.

We have seen that, considered roughly, the fluorescent spectrum covers the region of absorption. An attempt was made to study the relation between the wave-length of the absorbed and emitted light by means of a Fuess monochromatic illuminator. This apparatus enables one to isolate a region of any width from a continuous spectrum, and to focus this light on the vapor.

Wave-Lengths. Å	Wave-Lengths. Å	Wave-Lengths. Å	Wave-Lengths. Å
6346.1	6461.0	6560.0	6657.0
6354.8	6664.4	6568.4	6663.5 strong
6364.8	6474.7	6576.0	6670.1 "
6374.4	6483.6	6584.2 very strong	6677.2 "
6383.9	6490.8	6590.4	6678.0
6393.7	6495.1	6593.0	6682.4
6400.7	6499.6	6596.5	6709.0 strong
6407.3	6508.0	6605.9	6715.8 "
6415.9 strong	6514.8	6615.2	6722.0 "
6423.7	6521.5	6624.3 strong	6748.2 "
6430.6	6527.9	6630.9 "	6761.9 "
6437.7	6537.1	6636.4	6667.6 "
6443.8 strong	6544.4 very strong	6641.6	
6453.9	6552.6	6648.9	

The method was to find by changing the wave-length of the exciting light the region of absorption which gave the maximum intensity of fluorescence, and by narrowing the slit of the illuminator as far as was consistent with the observation of the fluorescence, to isolate if possible an approximately monochromatic source of excitation. The wave-length of the exciting light was increased by turning the graduated screw which rotated the prism of the instrument, and it was found that there was a wide region which would excite the fluorescence. The spectrum examined with the Steinheil spectroscope was, however, so feeble as to be hardly observable and little was derived from this method of study.

The zinc arc was then tried as a monochromatic source. The light from the arc formed in air between a carbon electrode and a small crucible into which pieces of zinc were fed, was brought to a focus just within the aperture of the retort containing the metal. This arc gave a very intense and strongly concentrated source of light, from which the single line 6363 was utilized. It was found that a strong fluorescence was excited by this line. Examined visually with a grating spectroscope a series of lines apparently equally spaced along the spectrum was observed, analogous to the series excited in sodium vapor by the blue cadmium line 4800.

The great difficulty of working with the arc in air is that the position of the crater changes constantly, making it almost impossible

to keep the spot of fluorescent light on the slit of the spectrograph for any length of time. The spectrum of the fluorescent light brought out by exciting with the zinc arc has not yet been photographed.

Absorption Spectrum.

The photographs of the absorption spectrum taken with the vapor in the bulb never showed very strong absorption for the reason that it was impossible to get the vapor sufficiently dense. With the steel tube it was possible to work with a very dense vapor, and with the greater dispersion given by the grating spectrograph, excellent photographs have been taken of the absorption spectrum.

A lump of potassium was placed at the center of the tube, the ends were cemented on and the tube exhausted as in the previous experiments. The tube was supported in a horizontal position in front of the slit of the spectrograph, and light from the arc sent through the tube was brought to a focus on the slit. By regulating the flow of gas to the burner, placed below and at the center of the tube, it was possible to observe the spectrum for any degree of density of the vapor. Photographs were taken at different densities. The heads of the bands appear first, and as the density increases the fine lines of which they are formed develop in succession. With a sufficiently dense vapor the spectrum consists of a very large number of fine black lines. The wave-lengths of the strong bands and principal lines of the absorption spectrum are given below.

Wave-Lengths. λ	Wave-Lengths. λ	Wave-Lengths. λ	Wave-Lengths. λ
6295.2	6399.7	6549	6675.1
6298.5	6412.5 strong	6559	6677.7
6306.8 strong	6420.3 "	6565.6	6709
6321.7	6433.8	6583.9 very strong	6714.5 strong
6324.6 strong	6443.3 very strong	6594.2	6721.4
6334.3 "	6466.8 " "	6605.0	6754.4
6343.3 "	6488.9 strong	6611.3	6759.9
6354.0 "	6505.3 "	6622.7 strong	6765.8
6362.9 very strong	6512.8 "	6629.4	6804.9
6370.1	6520.3 "	6641.2	6811.4
6382.9 very strong	6534.6	6662.7 strong	6849.9
6391.3	6544.3 very strong	6668.5 "	6855.5

MAGNETIC ROTATION SPECTRUM.

Method and Apparatus.—The magnetic rotation properties of potassium vapor were first investigated in the following way: A glass bulb which had been filled, exhausted and sealed off was suspended between the conical pole pieces of a large electromagnet. Light from an arc lamp rendered parallel by a lens was passed in succession through a nicol prism, the hollow cores of the magnet with the bulb containing the metal, and a second nicol, after which it was brought to a focus by a second lens on the slit of the grating spectroscope. The nicols were set for complete extinction of the light so that the field was dark. The bulb was heated by a Bunsen flame until the metal was vaporized, and the magnet excited. On looking into the spectrograph a faint yellow light was observed in the vicinity of the D lines due to rotation by traces of sodium vapor. No rotation lines in the red were observed. On repeating the experiment, however, with the vapor in a steel tube, a bright line rotation spectrum was discovered.

A piece of steel tubing of such diameter as to slip through the hollow cores of the magnet from which the conical pole pieces had been removed was charged with potassium and exhausted. Parallel light was sent through the tube, nicols, etc., as described above, and focused on the slit. With the current off the height of a flame placed beneath the center of the tube was regulated so that the absorption lines were brought out strong and black. The nicol was then set for complete extinction. On exciting the magnet there appeared in addition to the bright rotation lines D_1 and D_2 a number of bright lines in the red. It was found that the rotation spectrum was very sensitive to changes in the density of the vapor. The least variation in the height of the flame would destroy the spectrum. Electrical heating of a porcelain tube containing the metal was tried, but it was found that the density could be kept more constant by working with a steel tube and heating with a flame.

Several photographs of the rotation spectrum were taken. About twenty-five lines could be measured on the best plate. One was taken with the absorption spectrum on the same plate and shows the eight strong lines which were mentioned in connection with the fluorescent spectrum. The plate shows that they coincide with the

strong heads of the absorption bands. Six of these strong lines could easily be picked out as a series of lines, very nearly equidistant along the spectrum. Their wave-lengths are:

λ		λ Differences.
6383.02		
		29.69
6412.71		
		30.69
6443.4		
		30.81
6474.21		
		30.85
6505.06	$\frac{60.54}{2}$	
		30.27
6565.6		

There are three strong lines which do not fall in this series:

6512.67 6543.88 6583.32

The other lines are all of about the same intensity. Their intensities do not depend upon the intensities of the corresponding absorption lines, a fact which was found to hold in the magnetic rotation spectrum of sodium vapor. Some of the strongest lines in this region show no rotation. The wave-lengths of the lines that could be measured are as follows:

λ	λ
6298.63	6443.4 strong
6306.86	6474.21 "
6313.29	6489.69
6325	6505.06 strong
6329.23	6512.67 "
6342.81	6543.88 "
6351	6556.5
6354.77	6565.61 strong
6383.02 strong	6583.32 "
6391.13	6601.7
6412.71 strong	6614.6
6420.43	6622.35

The results obtained up to the present time can only be considered as preliminary in their nature. The vapor of potassium resembles that of sodium in its optical properties, but its study is attended by far greater difficulties. The banded absorption spectrum which gives rise to the fluorescence is located with respect to the first doublet of the principal series 7699 and 7665 in very much the same way as the sodium absorption spectrum is located with respect to the *D* lines. The marked resemblance in the

appearance of the spectra has been mentioned. Further work will doubtless show us ways of overcoming some of the difficulties, although it is very doubtful if we can ever handle the vapor with the same facility as is possible in the case of sodium, for there are very few sources of monochromatic red light available.

Careful study of the magnetic rotation spectrum will probably be more profitable, especially an investigation with the Fresnel double quartz wedges, which enable us to determine the direction of the rotation at each absorption band.

THE FREQUENCY OF THE SINGING ARC.

By George W. Nasmyth.

EVER since the discovery by Duddell[1] in 1900 that a direct current arc between solid carbons will give forth a musical note of high pitch if a circuit containing inductance and a suitable capacity is shunted across the arc, the question of the frequency of the oscillations in the shunt circuit has been of increasing interest and importance. In 1903 Poulsen[2] proposed the use of the singing arc in hydrogen as a source of undamped electric oscillations, and later[3] applied it successfully to wireless telephony, leading to a renewed interest in the problem of the frequency of the oscillations. In all more than a dozen investigators have considered the problem. It is the purpose of this communication to summarize briefly the work of these investigators in so far as it bears on the problem of the frequency, and to derive a formula, based on the known properties of the electric arc, which agrees with and explains the data thus far obtained.

The first assumption, based on the analogy with the oscillatory discharge of a condenser through a spark gap, was that the oscillatory current would obey the laws derived by Lord Kelvin[4] in 1853 in his classic paper, "On Transient Electric Currents," for the discharge of a Leyden jar. According to these laws, the frequency should be

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC} - \frac{R^2}{4L^2}},$$

where L is the inductance, C the capacity, and R the resistance of the oscillatory circuit. In general, since R is usually small, the

[1] W. Duddell, Journ. Inst. Elec. Eng., vol. 30, p. 232, 1900.

[2] V. Poulsen, British Patent Specification 15599 of 1903. See also Science Abstracts, vol. 8A, p. 521.

[3] V. Poulsen, Elektrotechnische Zeitschrift, vol. 27, p. 1040, 1906.

[4] Prof. William Thomson, Philosophical Magazine, ser. 4, vol. 5, p. 393.

second term under the radical is small compared with the first, and the frequency is given to a close approximation by the formula

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC}}.$$

Thus, in 1902, when M. Janet[1] published a mathematical treatment of the singing arc, he assumed as one of his premises that the frequency of the oscillations was determined by the formula

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC}}$$

and derived his results partly from this basis, taking it for granted that the values of L and C would be such that the effects of the capacity and inductance would neutralize each other.

Janet's assumption was immediately challenged by several Italian physicists, and A. Banti[2] proved that the frequency is not the same when the capacity and inductance are varied inversely as one another. He found that with an inductance of 0.048 henry and a capacity of 1 microfarad, the frequency was 13,000. With an inductance of 0.012 henry and a capacity of 4 microfarads the frequency was 8,500. With an inductance of 0.003 henry and a capacity of 16 microfarads, the frequency is 2,750. The frequency therefore increases with the inductance, even when the product LC is kept constant, and Banti's results proved that the frequency is not determined by the simple formula

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC}}.$$

In 1903 Duddell[3] pointed out that since the full expression for the frequency is given by the expression

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC} - \frac{R^2}{4L^2}}$$

[1] P. Janet, Comptes Rendus, vol. 134, p. 821, 1902.

[2] A. Banti, Elettricista, vol. 12, p. 1, Jan., 1903. See also L'Elettricità, Mar. 8, 1908, p. 145.

[3] W. Duddell, The Electrician, vol. 51, p. 902, 1903.

it follows that the frequency will be determined by the current and the arc length since the resistance is a function of both these variables. No numerical values were given, however, in confirmation of this opinion. As a matter of fact, even if the entire fall of potential across the arc is taken as representing resistance, this formula accounts for only a small percentage of the observed changes of frequency with arc length, arc current, and inductance.

In 1904, Maisel,[1] summarizing the results obtained by Corbino,[2] Salomonson,[3] and Ascoli and Manzetti,[4] stated the negative conclusion that the frequency is not determined by the simple formula

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC}}.$$

Maisel himself found that the frequency increased with the arc current, and the following data, due to him, are given in the same paper: $A = 3.8$ amperes, $T = 0.00075$ sec.; $A = 3.0$, $T = 0.000788$; $A = 2.05$, $T = 0.000800$; $A = 1.75$; $T = 0.000835$. Salomonson also had found that the frequency increased with increasing arc current. He did not determine the frequency directly, however, but computed it from a formula due to Peukert[5]

$$n = \frac{I_2}{2\pi C\sqrt{E_2^2 - E_1^2}},$$

in which C is the capacity in the shunt circuit, I_2 is the alternating current, E_1 is the voltage as determined by a d.c. voltmeter, and E_2 the voltage determined by a hot wire voltmeter across the arc. Salomonson's curves are of a different form from those of Maisel, Austin and the author, in which the frequency was determined directly by

[1] S. Maisel, Physikalische Zeitschrift, vol. 5, p. 550, 1904. See also French abstract in L'Eclairage Electricque, vol. 41, p. 186, 1904.

[2] O. M. Corbino, Atti dell'Associazione Ellettrot. Italiana, vol. 7, p. 369, also p. 597. See also Science Abstracts, vol. 7A, p. 537.

[3] J. Wertheim Salomonson, Koninklijke Akademie van Wettenschappen, Amsterdam, Versl. 1902–3, p. 381. See also his letter in The Electrician, vol. 51, p. 752, and Maisel's article, cited above.

[4] Ascoli e Manzetti, Rend. Acc. Lincei, 1902, 2° sem., fasc. 1°. See also M. La Rosa's article, cited later.

[5] W. Peukert, Elektrotechnische Zeitschrift, vol. 22, p. 467, 1901.

resonance, so that it is evident that Peukert's formula gives incorrect results for this case.

Simon and Reich[1] have experimented extensively on the singing arc, and H. Th. Simon[2] found that with low frequency arcs the frequency increases with increasing current and with decreasing arc length. M. La Rosa[3] has also considered the question of the frequency, but only incidentally, his chief interest being in the amplitude.

In 1907, L. W. Austin[4] published his experiments, showing, in agreement with Maisel, that the frequency of the oscillations increases with the arc current. Austin's curves show that the frequency increases rapidly at first, then more slowly, approaching

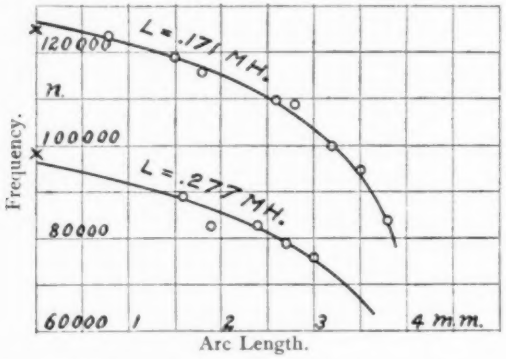

Fig. 1. Change of frequency with arc length. Frequency computed from formula $n = \frac{1}{2\pi}\sqrt{\frac{1}{LC}}$ marked $\times$.

an asymptote as the arc current becomes very large. Austin's experiments also indicated that the frequency increases with decreasing arc length, but no quantitative results were given showing this relation on account of the experimental difficulties met in trying to measure the change of arc length through the very limited range obtained.

CHANGE OF FREQUENCY WITH ARC LENGTH.

The author has undertaken a series of experiments to fill the gap existing in the data connecting the frequency with the arc length.

[1] Simon und Reich, Physikalische Zeitschrift, vol. 3, p. 278, 1902; vol. 4, p. 364, 1903.

[2] H. Th. Simon, Physikalische Zeitschrift, vol. 7, p. 433, 1906.

[3] M. La Rosa, Nuovo Cimento, vol. 7, p. 5, Jan., 1904.

[4] L. W Austin, Bulletin of the Bureau of Standards, vol. 3, p. 325, May, 1907.

The results of these experiments are given in Table I., and graphically in Fig. 1. These experiments show that the frequency de-

TABLE I. (Fig. 1.)

Change of Frequency with Arc Length. Primary Inductance, Including Connecting Wires, .171 *Millihenry. Primary Capacity,* 5 *Small Leyden Jars,* .00188 *Each,* .00940 *Microfarad. Computed Frequency from Formula* $n = \frac{1}{2\pi}\sqrt{1/LC} = 125{,}000$. *Secondary Inductance* .189 *Millihenry. Secondary Capacity Variable. P.d. Across Arc, Open Circuit,* 500 *Volts. Current in Secondary at Resonance, About* 10 *Amperes.*

Arc Length.	Volts.	Amperes.	Secondary Capacity.	Frequency.
3.8 mm.	160	1.75	.0186 microfarad	83,400
3.5	132	1.93	.0149	94,200
3.2	120	2.00	.0132	99,900
2.8	94	2.16	.01128	108,300
2.6	90	2.18	.01115	109,100
1.8	82	2.22	.00998	115,100
1.5	68	2.31	.00940	118,700
.8	60	2.40	.00871	123,200

Primary Inductance .277 *m.h. Computed Frequency,* $1/2\pi\sqrt{LC} = 98{,}000$.

3.0	134	1.80	.0201 m.f.	.219 millihenry	75,500
2.7	116	1.87	.0187	.219	78,300
2.4	108	1.91	.0169	.219	82,300
1.9	94	1.98	.0187	.189	82,500
1.6	84	1.98	.0169	.189	88,500

Other constants same as those above.

creases with increasing arc length, slowly at first, and more rapidly as the arc length is increased to three or four millimeters. For zero arc length, the curve cuts the axis of frequencies at the point corresponding to the frequency as computed from the formula

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC}}$$

a small difference of less than 2 per cent. being due to the influence of errors of observation. The conditions under which these observations were made are given in more detail below.

SUMMARY OF REQUIREMENTS.

An adequate formula for the frequency of the singing arc, then, in order to explain these results, must show: that the frequency increases with the inductance when the product of capacity and inductance is kept constant; that the frequency increases with increasing current through the arc; and that the frequency decreases with increasing arc length. To agree with the observations of the experimenters mentioned above, such a formula should show in addition that the curves of frequency become asymptotic for infinite inductance, infinite arc currents, and zero arc length.

In the following derivation of a formula for the frequency of the singing arc, Ohm's and Kirchhoff's laws are applied to the shunt circuit across the arc, and the known relations between the arc current and the potential difference across the arc are used.

DERIVATION OF FORMULA.

If I represents the the total current supplied to the circuit shown in Fig. 2, A the current through the arc, and i the current in the shunt circuit at any instant, the application of Kirchhoff's first law at the point P gives the relation

$$A + i = I. \tag{1}$$

If the inductance of the choke coil in the main circuit is sufficiently large, we may assume, as the experiments of the author have shown, that the main current I is appreciably constant. Differentiating equation (1), we have

$$\frac{dA}{dt} + \frac{di}{dt} = 0,$$

whence

$$\frac{dA}{dt} = -\frac{di}{dt}. \tag{2}$$

The relation between the potential difference across the arc V, and the current A through the arc, has been shown by Mrs. Ayrton[1] to be

$$V = a + bl + \frac{c + ld}{A^2}, \tag{3}$$

[1] Hertha Ayrton, The Electric Arc, p. 205.

where l is the length of the arc, and the constants a, b, c and d depend upon the electrodes between which the arc is formed and the nature and pressure of the surrounding gas. If we differentiate equation (3) with respect to A, we obtain the equation

$$\frac{dV}{dA} = -\frac{c + ld}{A^2}. \tag{4}$$

When the shunt circuit is closed, a current i flows in the direction indicated by the arrow, and we can apply Ohm's law to that part of

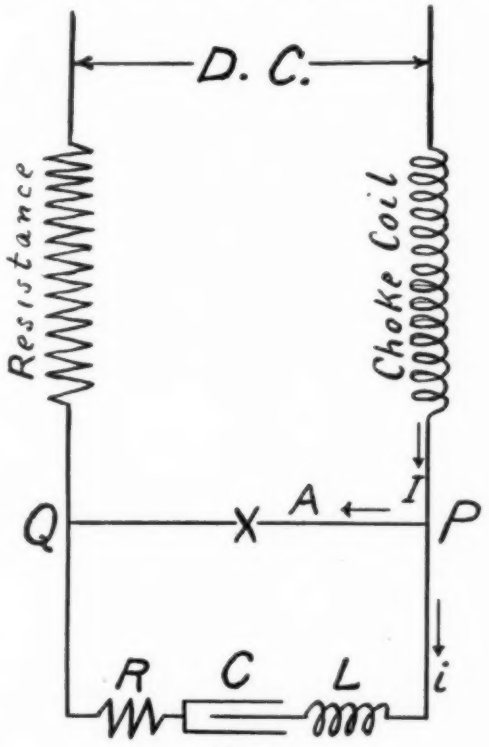

Fig. 2.

the condenser circuit between the points P and Q. The potential difference V between the points P and Q is used in three ways: to overcome the resistance of the condenser circuit, to overcome the inductance, and to charge the condenser. Stated mathematically, this is

$$V = Ri + L\frac{di}{dt} + \frac{q}{C}, \tag{5}$$

where V is the potential difference between the points P and Q across the arc, R is the resistance, L the inductance and C the capacity of the shunt circuit, and i and q are the instantaneous values of the shunt current and condenser charge respectively. Differentiating equation (5), it becomes

$$\frac{dV}{dt} = R\frac{di}{dt} + L\frac{d^2i}{dt^2} + \frac{1}{C}\frac{dq}{dt}. \tag{6}$$

The following relation is also true

$$\frac{dV}{dt} = \frac{dV}{dA}\cdot\frac{dA}{dt}. \tag{7}$$

Substituting the values of dV/dA and dA/dt from equations (4) and (2) in equation (7), we have

$$\frac{dV}{dt} = -\frac{c+ld}{A^2}\cdot\left(-\frac{di}{dt}\right)$$

or

$$\frac{dV}{dt} = \frac{c+ld}{A^2}\cdot\frac{di}{dt}. \tag{8}$$

Substituting the value of dV/dt from equation (8) in equation (6), we have

$$\frac{c+dl}{A^2}\cdot\frac{di}{dt} = R\frac{di}{dt} + L\frac{d^2i}{dt^2} + \frac{1}{C}\frac{dq}{dt}.$$

Transposing and grouping like terms,

$$L\frac{d^2i}{dt^2} + \left(R - \frac{c+ld}{A^2}\right)\frac{di}{dt} + \frac{1}{C}\frac{dq}{dt} = 0.$$

Since $i = dq/dt$, we may write this equation

$$L\frac{d^2i}{dt^2} + \left(R - \frac{c+ld}{A^2}\right)\frac{di}{dt} + \frac{i}{C} = 0. \tag{9}$$

Equation (9) is a well-known differential equation if the coefficient of di/dt is constant, *i. e.*, if the shunt current i is so small in comparison with the arc current A that A may be considered constant, or if a mean value of A is used. The solution of equation (9) when the coefficients are taken as constants, is found by assuming the

solution to be of the form $i = Be^{jpt}$, and determining the values of the constants B and p. The solution for the current i at any instant is found to be

$$i = Q\varepsilon^{-\frac{\left(R-\frac{c+ld}{A^2}\right)}{2L}t} \times \left[\frac{1}{LC\sqrt{\frac{1}{LC}-\frac{\left(R-\frac{c+ld}{A^2}\right)^2}{4L^2}}}\right] \sin \sqrt{\frac{1}{LC}-\frac{\left(R-\frac{c+ld}{A^2}\right)^2}{4L^2}}\cdot t. \quad (10)$$

From this expression the periodic time is found to be

$$T = \frac{2\pi}{\sqrt{\frac{1}{LC}-\frac{\left(R-\frac{c+ld}{A^2}\right)^2}{4L^2}}}$$

and the frequency

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC}-\frac{\left(R-\frac{c+ld}{A^2}\right)^2}{4L^2}}. \quad (11)$$

The Frequency as a Function of dV/dA, the So-called Negative Resistance of the Arc.

The expression (11) derived above, may also be derived by using what has sometimes been called the negative resistance of the arc, dV/dA. If we consider the whole resistance of the oscillatory circuit to be $(R + dV/dA)$, we find for the frequency,

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC}-\frac{\left(R+\frac{dV}{dA}\right)^2}{4L^2}}, \quad (12)$$

an expression identical with (11), since

$$\frac{dV}{dA} = -\frac{c+ld}{A^2}$$

from equation (4).

The formula (11) has been derived on the assumption that the characteristic curve between the p.d. and the current of the arc is the same when an alternating current is superimposed upon the direct current through the arc as for the direct current alone. If the frequency of the superimposed alternating current is high, it may be shown theoretically and verified experimentally (Fig. 3)

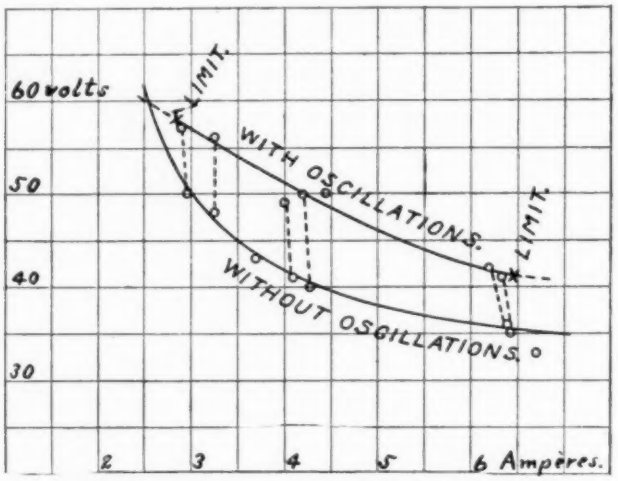

Fig. 3. Curves showing change in arc characteristic when oscillations traverse the arc. Corresponding points are connected by dotted lines and limits within which oscillations can be obtained are indicated.

that the curve representing the law of variation between the arc p.d. and current undergoes a change of form when the oscillations are allowed to pass through the arc. The formula (11) therefore requires modification for the high frequency case.

The change in the arc characteristic is probably due chiefly to the "skin effect" of high frequency currents. The high frequency currents are not distributed uniformly in the cross-section of the arc vapor, but are concentrated at the surface. The equivalent resistance of the arc vapor will therefore be greater for the high frequency currents than for the steady or low frequency currents. Lord Rayleigh[1] has derived the following formula for the resistance R' of a conductor to high frequency currents, the frequency n be-

[1] Lord Rayleigh, Philosophical Magazine, ser. V., vol. 21, p. 381, May, 1886. See also J. A. Fleming, The Principles of Electric Wave Telegraphy, p. 91.

ing of the order of 10^6, R being the steady current resistance, and d being the diameter of a circular sectioned conductor of non-magnetic material and of specific resistance ρ.

$$R' = Rd\frac{\pi}{2}\sqrt{\frac{n}{\rho}}. \tag{13}$$

This formula shows the high frequency resistance R' to be directly proportional to the diameter, d, of the arc and proportional to the square root of the frequency. Mrs. Ayrton[1] has shown that the square of the diameter of the arc crater and of the arc mist and vapor are very nearly proportional to the arc current. We may say then that the diameter of the conductor in this case is proportional to the square root of the current, and leaving out of consideration for the time being the change of resistance with frequency, we may write equation (13) thus,

$$R' = kR\sqrt{A},$$

where k includes all the other factors of equation (13) and Mrs. Ayrton's proportionality constant. Writing dV'/dA and dV/dA in place of R' and R, and substituting the value of dV/dA from equation (4),

$$\frac{dV'}{dA} = \frac{dV}{dA}k\sqrt{A} = -\frac{(c+ld)k\sqrt{A}}{A^2} = -\frac{c+ld}{A^{\frac{3}{2}}}, \tag{14}$$

where c and d in the last term have new values. Since the value of dV/dA is squared in the formula (12) the change introduced in formula (11) for the high frequency case is that A enters as a three halves power, and being squared becomes a nine fourths power, or practically A^2.

Several unconsidered factors, including the arc hysteresis, the heating at the edge of the arc crater due to the "skin effect," and the slight curvature toward the axis of mean cross-section of the arc mist in Mrs. Ayrton's curves, indicate that a closer approximation to the true law of the arc for the high frequency case should be

$$\frac{dV'}{dA} = \frac{c+ld}{A}. \tag{15}$$

[1] Hertha Ayrton, The Electric Arc, pp. 401 and 420, Fig. 133.

A test for this is found by integrating into the form

$$V = (c + ld) \cdot \log A + (a + bl), \tag{16}$$

from which it follows that the curve between the arc voltage and the logarithm of the arc current should be a straight line. Fig. 4,

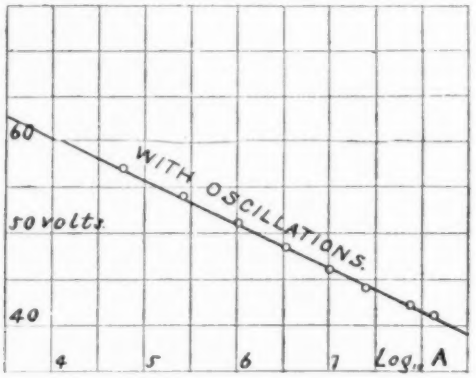

Fig. 4. Curve from data of Fig. 3, showing that for high frequency oscillations $V = (c + ld) \cdot \log A + (a + b)$, whence $\frac{dV}{dA} = -\frac{c + ld}{A}$.

the data for which are taken from the curve marked "with oscillations," in Fig. 3, shows that this is the case. For high frequencies therefore, the formula should be modified to the form

$$n = \frac{1}{2\pi} \sqrt{\frac{1}{LC} - \frac{\left(R - \frac{c + ld}{A}\right)^2}{4L^2}}. \tag{17}$$

This expression shows the frequency to be a function not only of the inductance and capacity L and C, and the resistance R of the oscillatory circuit, but of the arc current A and the length of the arc l as well. When further analyzed, the frequency is seen to be a function of the constants c and d also, depending upon the nature of the electrodes and the nature and pressure of the gas in which the arc is formed. The constants c and d are not the same when an alternating current is superimposed upon the direct current through the arc as they are when the direct current alone is flowing, in fact, dV/dA has itself been shown to be a function of the

frequency of the superposed oscillations, and is not a constant during one complete oscillation, owing to the phenomenon of hysteresis in the arc characteristic. To derive an exact expression for the frequency, taking into account all these variables, would be a tedious, if not impracticable process, and it has been thought better to leave the expression (17) in its present form, determining the constants by experiment. For nearly all practical purposes, the approximate formula (17) is of greater value than the much more complicated exact formula would be.

In general if we assume that the value of the constant c is small, so that both R and c may be neglected, we get, as an approximation not quite so close, the more convenient working formula

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC} - \frac{l^2d^2}{4L^2A^2}}. \qquad (18)$$

The constant d for high frequency oscillations is much larger than for a steady direct current through the arc. For certain critical cases the R and the c become important, and it should be noted that for high frequencies and large wires the value of R may be ten or more times its steady current value, on account of the "skin effect."

Verification of the Formula.

Before proceeding to the more rigid quantitative test of the formulas (17) and (18), it should be noted that qualitatively the expression for the frequency

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC} - \frac{l^2d^2}{4L^2A^2}}$$

agrees with and explains all the data that have been published thus far on the frequency of the singing arc. From the form of the equation, it is seen that if the inductance L is increased, while the product of the inductance and the capacity is kept constant, the second term under the radical will become smaller, and the frequency will increase, approaching an asymptote. This is in agreement with the results obtained by A. Banti, referred to above.

If the steady current through the arc A is increased, the second

term under the radical is decreased, and the frequency should increase, approaching an asymptote as the value of the second term under the radical approaches zero. This agrees with the results obtained by Maisel and by Austin. Moreover, if the change in arc current is produced by changing the arc length, since a relatively small increase in current results from a large decrease in arc length and both these effects work in the same direction, the increase of frequency as a function of the increase of current should in this case be much more marked. This also is in agreement with Austin's results.

Lastly, if the arc length is increased the second term under the radical becomes larger, and the frequency should decrease. For zero arc length the frequency should be that calculated by the simple formula

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC}}.$$

This is confirmed by the experiments of the author, shown graphically in Fig. 1.

For a more rigid test, the formula (18) may be put into more convenient form by squaring both members of the equation. It becomes then

$$n^2 = \frac{1}{4\pi^2 LC} - \frac{l^2 d^2}{16\pi^2 L^2 A^2}.$$

If the formula agrees with the experimental data, a straight line should result if any of the following plots are made, n^2 against l^2, n^2 against $1/A^2$, or n^2 against l^2/A^2, all the other quantities being kept constant in each case.

Author's Data. — In Fig. 5 the curves shown in Fig. 1 have been replotted in the straight line form, n^2 against l^2/A^2. The original data are given in Table I., and the computations in Tables II. and III. The agreement with the straight line required by the theory is seen to be very close, easily within the errors of observation. For points close to the Y-axis the influence of the neglected quantities c and R of expression (17) is apparent. For the same reason

the Y intercept differs slightly from the theoretical value found from the simple formula

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC}}.$$

The straight line corresponding to the smaller inductance is seen to have the greater slope, numerically, corresponding to the fact that L appears in the denominator of the expression for the slope,

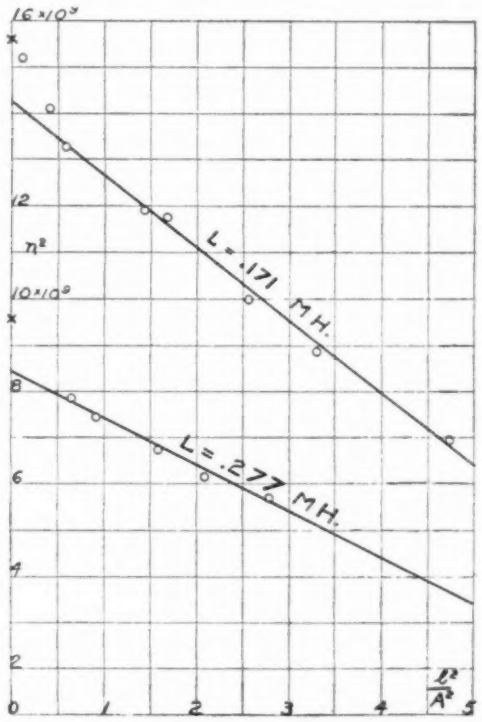

Fig. 5. Curves from author's data. Equation of straight lines,

$$n^2 = -\frac{d^2}{16\pi^2L^2}\cdot\frac{I^2}{A^2} + \frac{1}{4\pi^2LC}.$$

$-d^2/16\pi^2L^2$. The value of the constant d from the upper curve is about 63, and from the lower curve about 78, giving a mean value of about 70, and apparently decreasing as the frequency increases.

Austin's Data.—The curves shown in Figs. 6 and 7, corresponding to Tables IV., V., VI. and VII. are from Austin's data, put

TABLE II. (Fig. 5.)

Change of Frequency with Arc Length and Arc Current. Primary Inductance, .171 Millihenry.

n	n^2	l. in mm.	A	I^2A^2
83,400	6.96×10^9	3.8	1.75	4.71
94,200	8.89	3.5	1.93	3.29
99,900	9.98	3.2	2.00	2.56
108,300	11.77	2.8	2.16	1.68
109,100	11.94	2.6	2.18	1.42
115,100	13.28	1.8	2.22	.659
118,700	14.10	1.5	2.31	.422
123,200	15.21	.8	2.40	.111

Frequency computed from formula $n = 1/2\pi\sqrt{1/LC} = 125{,}000$.

TABLE III. (Fig. 5.)

Primary Inductance, .277 Millihenry.

n	n^2	l. in mm.	A	I^2A^2
75,500	5.70×10^9	3.0	1.80	2.78
78,300	6.13	2.7	1.87	2.09
82,300	6.79	2.4	1.91	1.58
86,100	7.41	1.9	1.98	.92
88,500	7.84	1.6	1.98	.65

Point at 1.9 mm. corrected from curve in Fig 1.
Frequency computed from formula $n = 1/2\pi\sqrt{1/LC} = 98{,}000$.

in the straight line form for the purpose of verifying the formula. The agreement with the straight line requirement is seen to be close in all the curves. In this case there is no error introduced through neglecting the constant c, because c appears in the numerator of the expression for the slope. The intercept should give the correct square of the frequency found by the simple formula assuming that the high frequency value of R is still small enough so that it may be neglected. The mean value as given by the three intercepts of the fundamental and two harmonics in Fig. 7 is 282,000. The value as calculated by Austin from the simple formula is 260,000, and as calculated from his data, 264,000. The value of L is given by Austin as "about 0.009 millihenry." To agree with the frequency as given by the intercepts, the value of the inductance must be 0.0079 mh. assuming the capacity to be

correctly given as 0.04 m.f. (misprinted in original article as 0.4 ohm). The correction for the high frequency inductance would be in the right direction to account for the difference, but an accurate determination of the constants of Austin's circuit would be an interesting test of the formula (17).

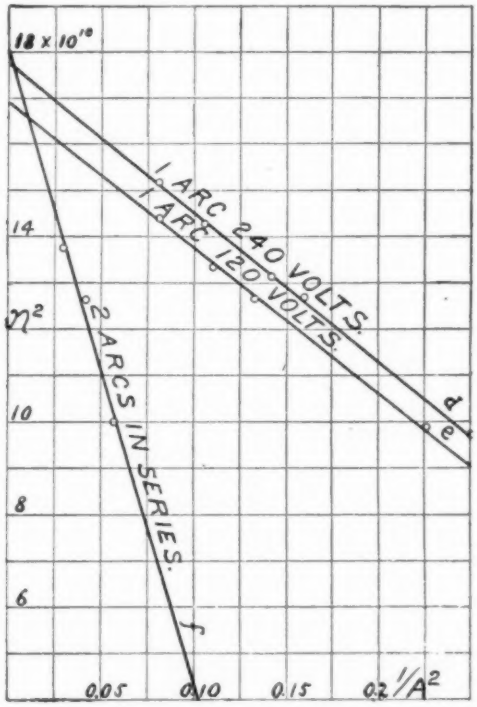

Fig. 6. Curves from Austin's data. Equation of straight lines,

$$n^2 = -\frac{(c+ld)^2}{16\pi^2L^2}\cdot\frac{1}{A^2}+\frac{1}{4\pi^2LC}.$$

In Fig. 6, the curve for the two arcs in series — corresponding to a greater arc length — has a greater slope than the curves for the single arcs, agreeing with the formula, since l appears in the numerator of the slope. The difference in the intercepts of the curves d and e is probably due to a small change in the primary inductance caused, perhaps, by shifting a wire, and cannot be due to a change in the arc length, as Austin suggests, since the slopes are unchanged.

The slopes in the curve shown in Fig. 7 are in the ratio 1 : 4 : 9 as are also the intercepts, indicating that the ordinates plotted are the squares of the ratios 1 : 2 : 3. This is in accordance with Austin's conclusion.

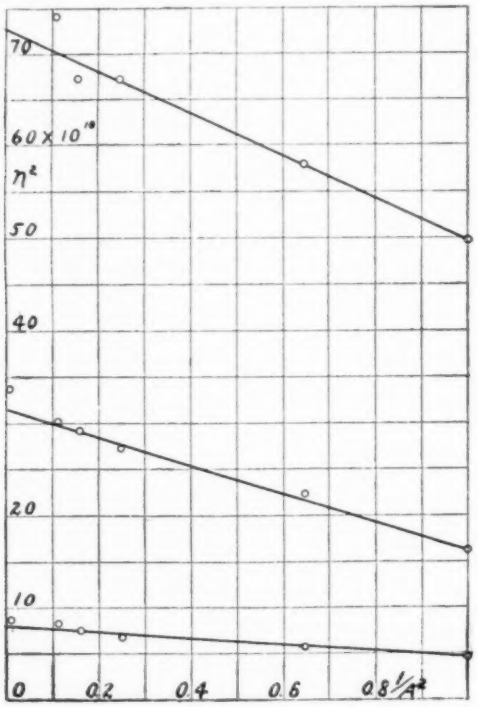

Fig. 7.

TABLE IV. (Fig. 6, Curve *d*.)

Current Changed by Changing Main Circuit Resistance.

n	n^2	A	$1/A^2$
312,000	9.74×10^{10}	2.0	.25
356,000	12.70	2.5	.16
378,000	14.28	3.0	.111
390,000	15.20	3.5	.082
420,000	17.61	5.2	.037

Frequency from *y*-intercept of curve, 424,000. 1 arc, 240 volts. Arc length about 0.3 mm.

TABLE V. (Fig. 6, Curve *e*.)

n	n^2	A	$1/A^2$
315,000	9.92×10^{10}	2.1	.227
356,000	12.68	2.8	.128
365,000	13.35	3.0	.111
379,000	14.40	3.5	.082

1 arc, 120 volts.

TABLE VI. (Fig. 6, Curve *f*.)

n	n^2	A	$1/A^2$
316,000	10.00×10^{10}	4.2	.057
355,000	12.61	5.0	.040
371,000	13.79	5.8	.0297

2 arcs in series, 240 volts.

TABLE VII. (Fig. 7.)

240-*Volt Circuit; p.d. Across Arc About* 34 *Volts. Current Changed by Changing External Resistance.*

n	n^2	A	$1/^2A$
217,000	4.71×10^{10}		
400,000	16.00	1 amp.	1
705,000	49.70		
236,000	5.58		
472,000	22.30	1.5	.444
760,000	57.80		
263,000	6.91		
520,000	27.1	2.0	.25
820,000	67.1		
274,000	7.50		
540,000	29.2	2.5	.16
820,000	67.1		
289,000	8.37		
550,000	30.2	3.0	.11
860,000	74.0		
295,000	8.71		
580,000	33.6	4.0	.082
910,000	82.9		

Points at 1.5 amperes have been interpolated from Austin's curves.

Maisel's Data. — The straight line curves corresponding to Maisel's data, taken in 1903, have been plotted by the author, but are not reproduced here, as they are of exactly the same nature as those of Austin. The straight lines from Maisel's data are interesting as showing that for frequencies even as low as 1,200 the formula (17) still holds true, a straight line resulting from the plot of n^2 against $1/A^2$, and not $1/A^4$, as might have been expected

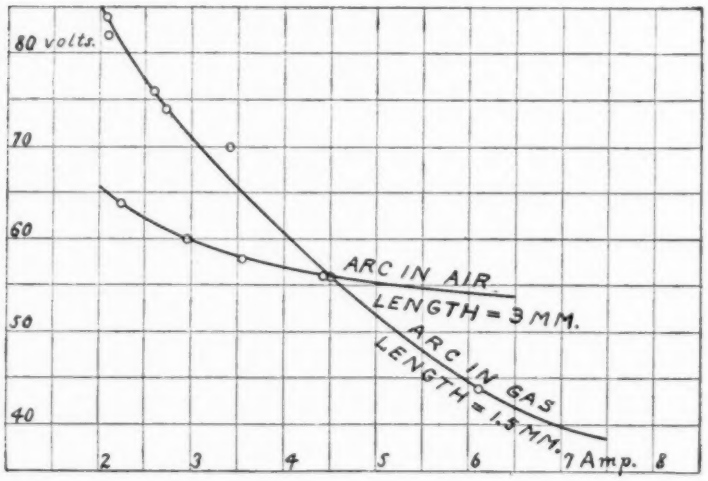

Fig. 8. Curves showing increase in $\frac{dV}{dA}$ for arc in gas.

for such low frequencies. The frequency as calculated from the inductance of 3.4×10^{-3} henrys and capacity of 3.43 m.f. is 1,460, while that given by the intercept is 1,360, a fairly close agreement, considering the irregular nature of the data.

Banti's data are not available for a check on the formula, only three points being given, and the range of frequencies being so great. It is considered that the change in slope in the author's experiments and those of Austin furnishes a better verification of the formula for the case of change of inductance.

The formula (17) and the approximation (18) may therefore be regarded as verified by all the data hitherto published on the frequency of the singing arc. The more exact determination of the constants c and d of the formula, as well as the manner in which d

changes with the frequency, must wait for further experiments. The formula (12) gives promise of being a potent instrument for determining the law of the variation of dV/dA with the frequency.

The manner in which dV/dA or its equal $(c + ld)/A$ enters into the exponent of the damping factor $\epsilon^{-[R-(c+ld)/A]t/2L}$ and into the expression for the amplitude is worthy of note. Since R is in general small compared with the second term in the exponent, the exponent as a whole is positive instead of negative, indicating that instead of the oscillations being damped they should continue to increase in amplitude. This goes on until the limit of the power that can be furnished by the arc is reached, when the oscillations settle down to equilibrium conditions, undamped, and not increasing. To get the maximum energy from the arc, it is evident that dV/dA must be as large numerically as possible, and negative. To fulfill these conditions, the arc should be as long as possible and the current as small as possible. The constants c and d can be made larger by having the electrode as good conductors of heat as possible, and by increasing the pressure of the surrounding gas, or forming the arc in an atmosphere of hydrogen or steam instead of in air. The increase in the slope of the curve for the arc in gas over that for the arc in air is shown graphically in Fig. 8 from the author's date. All these conditions may be summarized by saying that $(c + ld)/A$ should be a maximum, and all the conditions specified above are confirmed by experiments.

Author's Experiments.

The experiments of the author have been made with a d.c. arc enclosed in a bronze chamber containing illuminating gas instead of hydrogen, the gas being constantly renewed. The anode was of copper, wedge-shaped and water-cooled, with its sharp edge turned toward a graphite disc of about two cm. radius forming the cathode. The graphite disc was turned slowly by a small motor working through two worm gears in series, giving a 10,000 : 1 reduction. At the slowest speed of the motor the disc made about one revolution in eighteen minutes, and the speed was adjusted so as to present a new surface on the graphite disc as it was burned away. The arrangement of apparatus was similar to that shown in Fig. 2, the

choke coil being the primary of a large transformer, designed to operate on 600 volts a.c., and the resistance being a large water rheostat, with other resistance frames in series. Steady conditions and a large range of operation were secured by a supply of 500 volts d.c. maintained at constant pressure by a Tirrell regulator. In addition to the apparatus shown in Fig. 2, a d.c. voltmeter was connected across the arc, a d.c. ammeter was placed in series with the resistance, and a secondary resonance circuit containing a variable inductance a variable capacity and a hot wire ammeter, was loosely connected with the inductance L.

The secondary inductance and capacity were calibrated by comparing them with certain standard forms, the inductance with long helices, rectangles and circles, and the capacity with circular plates. In calibrating the capacity Kirchhoff's formula

$$C = \frac{\pi r^2}{4\pi d} + \frac{r}{4\pi d}\left\{ d \log_\epsilon \frac{16\pi r(d+t)}{\epsilon d^2} + t \log_\epsilon \frac{d+t}{t} \right\},$$

where r is the radius, t the thickness and d the distance apart of the plates, was used, correcting for the thickness and edge effects of the circular plates. The equivalent inductance of the primary and secondary circuits was determined by measuring the inductance of circuits of the same area made of the same sized wire.

In measuring the arc lengths, the method of direct determination was used, the arc being extinguished after each determination of the frequency, and the distance between the edge of the anode and the graphite disc measured with a scale and calipers.

The method of operation was to set the secondary circuit for the desired frequency, and then tune the primary circuit to resonance with the secondary by increasing the length of the arc. The final adjustments were made with the variable capacity in the secondary.

The author has confined himself, as far as possible, to the question of the frequency in this communication, and a more detailed description of his apparatus is unnecessary at present. The author hopes later to publish a contribution to the study of the symmetry and the energy relations in the singing arc, and to give a more detailed description of his apparatus and instruments at that time.

SUMMARY.

The frequency of the singing arc is not determined by the simple formula

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC}}.$$

The frequency increases with the inductance when the product of the inductance and capacity is maintained constant, and the curve of frequency approaches an asymptote when the inductance is made very large.

The frequency increases when the steady current through the arc is increased, and approaches as an asymptote the value given by the formula

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC}}$$

when the current becomes very large.

The frequency decreases when the length of the arc is increased and for zero arc length the frequency is given by the formula

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC}}.$$

The frequency is decreased by surrounding the arc by gas instead of by air, and by increasing the pressure of the air or gas.

The correct formula for the frequency of the singing arc

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC} - \frac{\left(R - \frac{c + ld}{A}\right)^2}{4L^2}},$$

which explains all the above effects, may be derived by using Ohm's and Kirchhoff's laws and the characteristic properties of the electric arc.

For purposes of calculating the formula may be written approximately

$$n = \frac{1}{2\pi}\sqrt{\frac{1}{LC} - \frac{d^2l^2}{4L^2A^2}}$$

and in this form agrees closely with the observed facts except in certain critical cases.

The formula may be written in a more general form as

$$n = \sqrt{\frac{1}{LC} - \frac{\left(R + \frac{dV}{dA}\right)^2}{4L^2}}$$

and in this form may be used to determine the change of dV/dA with the frequency.

In practical application, the formula shows that when a large change of frequency is desired with a small change of arc current, as in certain systems of wireless telephony, the inductance L of the shunt circuit should be very small. If steady conditions of tuning are desired, L should be large, thus making the effect of the second term under the radical small.

In order to secure a maximum of energy in the oscillations, dV/dA should be negative and as large numerically as possible. In other words, $(c + ld)/A$ should be a maximum. To satisfy this condition, the arc length should be large, the arc current small, the arc should be formed in gas or in air under pressure, and the electrodes and enclosing chamber should be of large heat capacity and good thermal conductivity.

PHYSICAL LABORATORY, CORNELL UNIVERSITY.

A GALVANOMETER SCALE FOR THE DIRECT READING OF TEMPERATURES WITH THERMO-ELECTRIC COUPLES.

By Anthony Zeleny.

IT is often desirable to use a direct-reading instrument when employing thermo-electric couples for the measurement of temperatures. An accurate scale for such an instrument can be constructed in the following manner:

From the general equation for thermo-electric couples, $e = at + bt^2$, it follows that the rate at which the electromotive force changes with the temperature, is

$$\frac{de}{dt} = a + 2bt.$$

At any temperature t, therefore, the electromotive force due to a difference of one degree in temperature is equal to $a + 2bt$. Since this electromotive force is different at different temperatures, the galvanometer deflections produced per degree vary with the temperature. The relative magnitudes of the scale divisions are then expressed by

$$D : D' :: a + 2bt : a + 2bt',$$

and

$$D' = \frac{a + 2bt'}{a + 2bt} D.$$

In this manner the length of the division D' at any temperature t' is calculated from the chosen length of the division D at the temperature t. The increments required for the intermediate successive scale divisions are equal and their value is $(D' - D)/(t' - t)$. The scale is ruled preferably on a dividing engine. The first division is made of the chosen magnitude D, and the succeeding divisions are each made larger than the one nearest preceding it by the amount of the above increment.

The proper resistance required for the galvanometer circuit is found by placing the two junctions each into one of two vessels of different temperatures. When the circuit is open, the scale is set to indicate the temperature of the junction that is intended to be used as the known temperature junction, and when the circuit is closed, resistance is introduced into the circuit until the galvanometer reads the temperature of the other junction. This is the proper resistance for temperature measurements with that galvanometer, scale and couple.

In any future measurements the scale is first set to indicate the temperature of the known temperature junction, then, when the circuit is closed, the temperature of the other junction is directly indicated by the galvanometer. A correct reading of the temperature is obtained regardless of what may be the temperature of the room or vessel containing the known temperature junction.

The scale may be drawn in sections, one under the other, enabling the whole range of measurable temperatures to be extended over a larger length. The known temperature junction must be maintained at some temperature that is contained in the particular section employed.

For precision measurements the defects inherent in galvanometers must be considered. In the moving coil type these are: (1) The variation in the proportionality of the deflection to the current; (2) hysteresis;[1] (3) thermo-electromotive force present within the galvanometer; (4) temperature coefficient[2] of the galvanometer. The effect of the thermo-electromotive force present within the galvanometer is avoided by having the galvanometer circuit closed, exclusive of the thermo-electric junction, while the scale is set to indicate the temperature of the known temperature junction, or, whenever it is convenient, by setting the scale while both junctions are at the same known temperature and the active circuit is closed.

The moving coil galvanometer with the above described scale has been employed[3] successfully by the writer for several years, and was

[1] A. Zeleny, PHYS. REV., Vol. 23, p. 399, 1906.

[2] A. Zeleny and O. Hovda, PHYS. REV., 1908.

[3] A. Zeleny, Engineers Year Book, Univ. of Minn., 1907; U. S. Patents Nos. 705186, 705187, 721770.

found to be convenient for many purposes. This method is especially useful in investigations where temperatures at several points are required. The several junctions, which have a common return branch and a common known temperature junction, are placed in succession in circuit with the galvanometer.

PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA,
February 21, 1908.

NEW BOOKS.

The Modern Theory of Physical Phenomena (Radioactivity, Ions, Electrons). By AUGUSTO RIGHI. Third edition. Bologna, Zanichelli.

Ionization and Electric Convection on Gases. By L. AMADUZZI. Bologna, Zanichelli.

These two books, consisting of about three hundred pages each of not very closely printed text, are numbers three and nine respectively of a series of scientific memoirs entitled "Attualità Scientifiche." This title, which it is difficult to translate into concise English, implies a treatment of the newer discoveries, in the various sciences, which have been carried so far as to leave little doubt but that the interpretation of the results is in the main correct and which are still so recent that they have not yet become matters of general knowledge.

The aim of the writers of these memoirs has been to give a popular treatment which should nevertheless be comprehensive enough to serve as a preparation for the study of the original memoirs. It is worthy of note that several editions have appeared in the case of some of these books which we on this side of the Atlantic would hardly classify as popular.

The third edition of Professor Righi's book preserves the form and order of presentation of the subject adopted in the earlier edition from which the English, French and German translations were made. Almost all of the chapters have been considerably amplified and a new chapter on atomic transformations in radio-active bodies has been inserted.

A very good feature of the book is the complete bibliography at the end which is presented in a form not necessarily requiring a knowledge of Italian to be of use to English readers.

It is unfortunate that Dr. Amaduzzi's book on Ionization is reviewed in this journal two years after its publication for it is necessary to call attention to omissions which are in nowise the fault of the author. Except for the recent experiments on ionization produced by radio-active bodies, anode rays, Townsend's measurements of the positive ions produced in air by Röntgen rays and Thomson's measurements of e/m for canal rays, all of which have been made since 1906, Dr. Amaduzzi's book gives a very thorough resumé of what is known at the present time in the matter of which he treats.

The presentation of the subject is clear and liberal use is made of diagrams and tables of experimental results. Considerable space is devoted to experiments on electric convection in gases at atmospheric pressure — a subject in which the Italian physicists have been, it would seem, pioneers.

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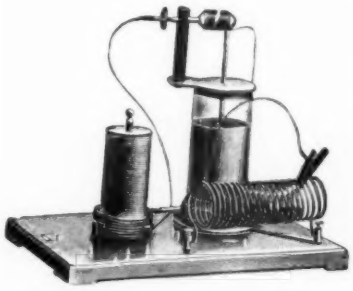

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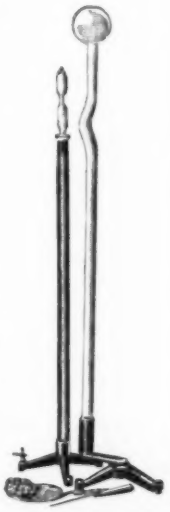

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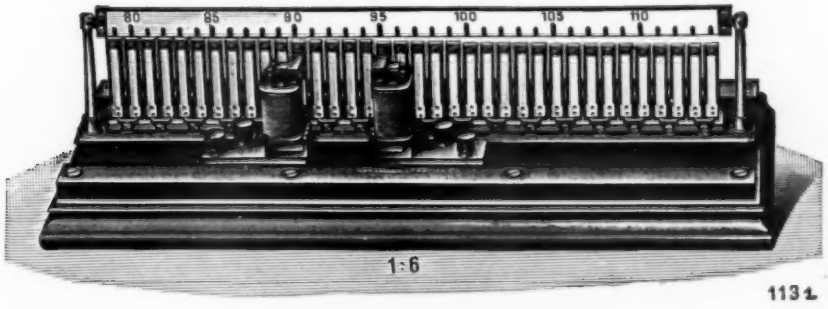

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